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Vapor phase ammoxidation of o-xylene over tungstate catalyst.

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VAPOR PHASE AMMOXIDATION OF o-XYLENE OVER TUNGSTATE CATALYST

A Thesis
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by

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ABSTRACT

Catalytic vapor phase ammoxidation of o-xylene was studied in a fixed bed integral reactor. Six catalysts were tested and a tungstate catalyst was found to be the most attractive. Further experiments were conducted with the tungstate catalyst to investigate its performance under different temperatures, ammonia/o-xylene mole ratios and contact times. The reaction products were analyzed by gas-chromatographic techniques developed during the course of this work.

The over-all rate of ammoxidation of o-xylene was found to be first order with respect to xylene concentration.

A number of kinetic models were tested for the over-all reaction scheme but none of them was found to give a totally satisfactory fit.

ACKNOWLEDGEMENTS

The author wishes to take this opportunity to express his sincerest appreciation to his advisors, Dr. G.P. Mathur and Dr. M. Adelman, for their encouragement and invaluable guidance throughout the course of this investigation, for their helpful suggestions and patience during the preparation of this thesis.

Gratitude is also extended to Dr. K.G. Rutherford for serving as member of his examination committee.

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I INTRODUCTION

Ammoxidation is a partial oxidation process in the presence of ammonia, which makes it possible in a single step to produce imides, amides, nitriles and other nitrogen-containing compounds directly from hydrocarbons.

Prior to World War II, all xylenes were produced from coal-derived sources. During the war time the petroleum industry was called upon to greatly expand its catalytic reforming facilities in order to provide the high octane fuel which was needed for aircraft engines and also to produce toluene which was needed for the manufacture of TNT. Continued postwar expansion of the reforming process to provide high octane gasoline components has made a reservoir of $C_6 - C_8$ aromatics potentially available for petrochemicals. At the present time, very large volumes of benzene, toluene and xylenes are produced by petroleum refiners. The xylene fraction is used as a source of solvents and for the production of seperated isomers. The production of xylenes over the past twenty-five years is shown in Figure 13, Appendix V. The production of individual isomers is shown in Figure 14, Appendix V.

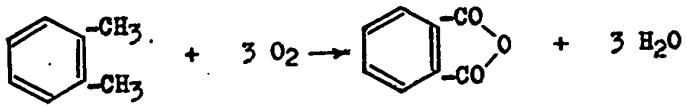
The current prices are shown in Table 8, Appendix V. It shows that o-xylene, at three cents per pound, is cheaper than other C_8 compounds.

A forecast of the aromatics demand through 1980 is given in Table 9, Appendix V.

Besides its use as a solvent, xylene is also used as a raw material in oxidation and ammoxidation reactions to produce more useful chemicals. The large capital investments involved provide the incentive for research in this

area. Numerous applications for them have been found in the production of synthetic fibres and film, plactics, resins and dyes.

Oxidation of o-xylene, for example, leads to the following products.



At present there are four fundamentally different reaction processes.

(1) Low temperature fixed-bed air oxidation of o-xylene

Reaction temperature is maintained in the range of 350 - 360 °C. with 4 - 5 seconds contact times. A high yield is obtained, with almost unlimited life time of the catalyst which is usually vanadium pentoxide on silica with 20 - 30 % potassium sulfate. This process produces 0.97 pounds phthalic anhydride per pound o-xylene (95 % purity).

(2) High temperature fixed-bed air oxidation of o-xylene

Temperatures are 400-475 °C. with 0.4 - 0.6 seconds contact times. The yield is lower than the above process, about 0.9 - 0.95 pounds phthalic anhydride per pound o-xylene (95 %), and the life of catalyst is limited. The reactor capacity is larger.

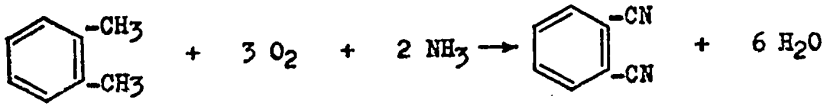
(3) Fluidized-bed air oxidation of o-xylene

o-Xylene gave unsatisfactory yields with catalysts available prior to 1967. By-products were excessive. However, plants as large as 33,000 - 36,000 tons/year presumably using a single reactor and ability to ultilize o-xylene were announced in 1966.

(4) Liquid-phase air oxidation process

This process is based upon a solvent system such as acetic acid and with a bromine-activated heavy-metal catalyst system and has been operated by AMOCO Chemicals Cooperation in the U. S. It incorporates oxidation of mixed xylenes to mixed phthalic, iso-phthalic and tere-phthalic acid. A liquid-phase oxidation process for o-xylene was also announced. The process has a considerable yield (1.3 lb. phthalic anhydride/lb. o-xylene) advantage over vapor-phase processes. It operates at 150 -250 °C., thus there is little lost of feedstock to carbon dioxide. This reduction in carbon dioxide formation also results in a considerably reduced heat-removal problem.

This investigation is concerned with process of type (2). In particular, ammoxidation of o-xylene is experimentally studied. The ammoxidation reaction follows, in main, the following reaction scheme



o-xylene phthalonitrile

The side products are o-tolunitrile and phthalimide.

The reaction process is in principle similar to the air oxidation of o-xylene. The major part of studies on the vapor phase ammoxidation of xylenes has dealt with the determination of the conditions for producing dicyano-benzenes. Several kinetic studies have been made with regard to the catalytic ammoxidation over vanadium oxide catalysts. The present study is an attempt to find out the influence of the main factors on the ammoxidation of o-xylene over a tungstate catalyst and is also an attempt to investigate some aspects of the reaction kinetics of this process.

II LITERATURE SURVEY

Very few exhaustive studies have been made on ammoxidation of o-xylene. There is somewhat more information on air oxidation of o-xylene. The following survey is divided in two parts, the first dealing with publications on ammoxidation of xylenes, and the second with publications of relevance for catalyst selection.

A. Vapor Phase Ammoxidation of Xylenes

Ammoxidation of substituted aromatic compounds was first carried out by Cosby et al. (2) in 1946, and the details of the reaction have since been reported in many papers and patents. Most of the attempts to obtain phthalonitriles with good yield have been made by improving reaction conditions or catalysts. Several kinetic studies have been made on the ammoxidation of xylenes over vanadium oxide and mixed catalysts.

Ito (14) studied in detail ammoxidation of o-xylene over vanadium oxide catalyst. These findings may be summarized as follows, in terms of factors affecting the oxidation.

(i) Reaction Temperature

The experimental results showed that the yield of phthalonitrile and phthalimide becomes greater as the temperature is increased in the range of 380 - 500 °C. The conversion to phthalonitrile decreases for temperatures higher than 485 °C. while that to phthalimide is increased.

(ii) Contact Time

Experiments were done at 470 ^{o}C. with a 0.4 - 7.5 seconds variation of contact. The experimental results showed that the formation rate of phthalonitrile and phthalimide are both increased by increasing the contact time, but the formation rate of o-tolunitrile is first increased and later decreased by increase of the contact time.

(iii) Concentration of Oxygen

Experiments were carried out at 470 - 485 ^{o}C., 500 hr^{-1} and a mole ratio of 5 (ammonia/o-xylene) with a mole ratio range (oxygen/ o-xylene) of 3 - 13. The result showed that if the mole ratio of oxygen to o-xylene is greater than 5, the effect of oxygen concentration is very small. However, for ratios less than 5, the formation rates of all products are decreased.

(iv) Concentration of Ammonia

Experiments were conducted at 478 - 491 ^{o}C. and 500 hr^{-1} with mole ratio of ammonia to o-xylene varied from 0 to 8. For mole ratio of ammonia to o-xylene greater than 5, the formation rates of phthalonitrile and phthalimide were found to remain constant.

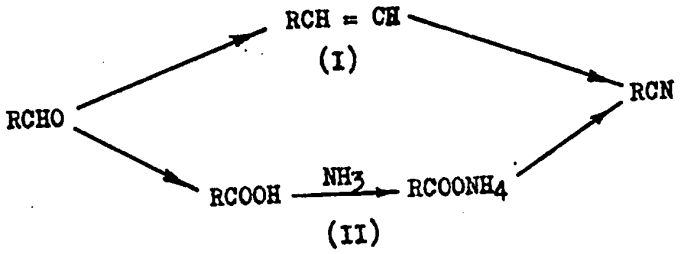
(v) Vapor Content

The experiments were performed at the same condition as in (iii) except that the air was used and ratio of steam to o-xylene varied over 0 - 22. The results showed that when the mole ratio of steam to o-xylene is increased, the formation rate of phthalimide is increased while that of phthalo-

nitrile is decreased.

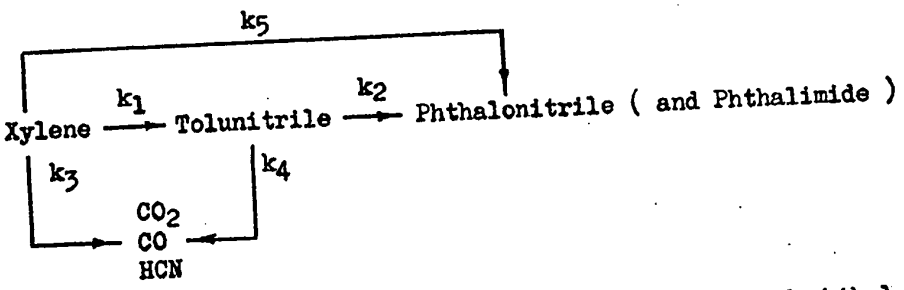
The kinetics and mechanism of vapor phase ammoxidation have been studied by Ito, Hadley and Suvorov (8, 15, 16, 17, 44). The suggestions of different investigators are quite different.

Hadley suggested that the reaction proceeds through the following two routes.



In a particular case the route will depend on the nature of R and, possibly, on the catalyst used. For the ammoxidation of acrolein over a molybdic oxide catalyst, route (I) is of major important. For the ammoxidations of alkyl aromatics over a catalyst containing a vanadium oxide, route (II) is more important.

Ito suggested that the rate controlling step in reaction is chemical reaction on the catalyst surface, i.e. the rates of adsorption of the reactants and of the desorption of the products are rapid. The reaction scheme suggested for the ammoxidation of xylene is



It was assumed that for the ammoxidation of o-xylene the sum of phthalonitrile

and phthalimide corresponded to the quantity of iso-phthalonitrile or tere-phthalonitrile.

Ito's treatment of data was based upon the Langmuir-Hinshelwood mechanism.

The rate expressions for the various steps in the above scheme were found to be as follows:

$$R_X = -\frac{dC_X}{dt} = k_X$$

$$R_T = \frac{dC_T}{dt} = k_1 - k_T P_T/P_X$$

$$R_P = \frac{dC_P}{dt} = k_5 + k_2 P_T/P_X$$

$$R_D = \frac{dC_D}{dt} = k_3 + k_4 P_T/P_X$$

where k Specific rate constant

P Partial pressure

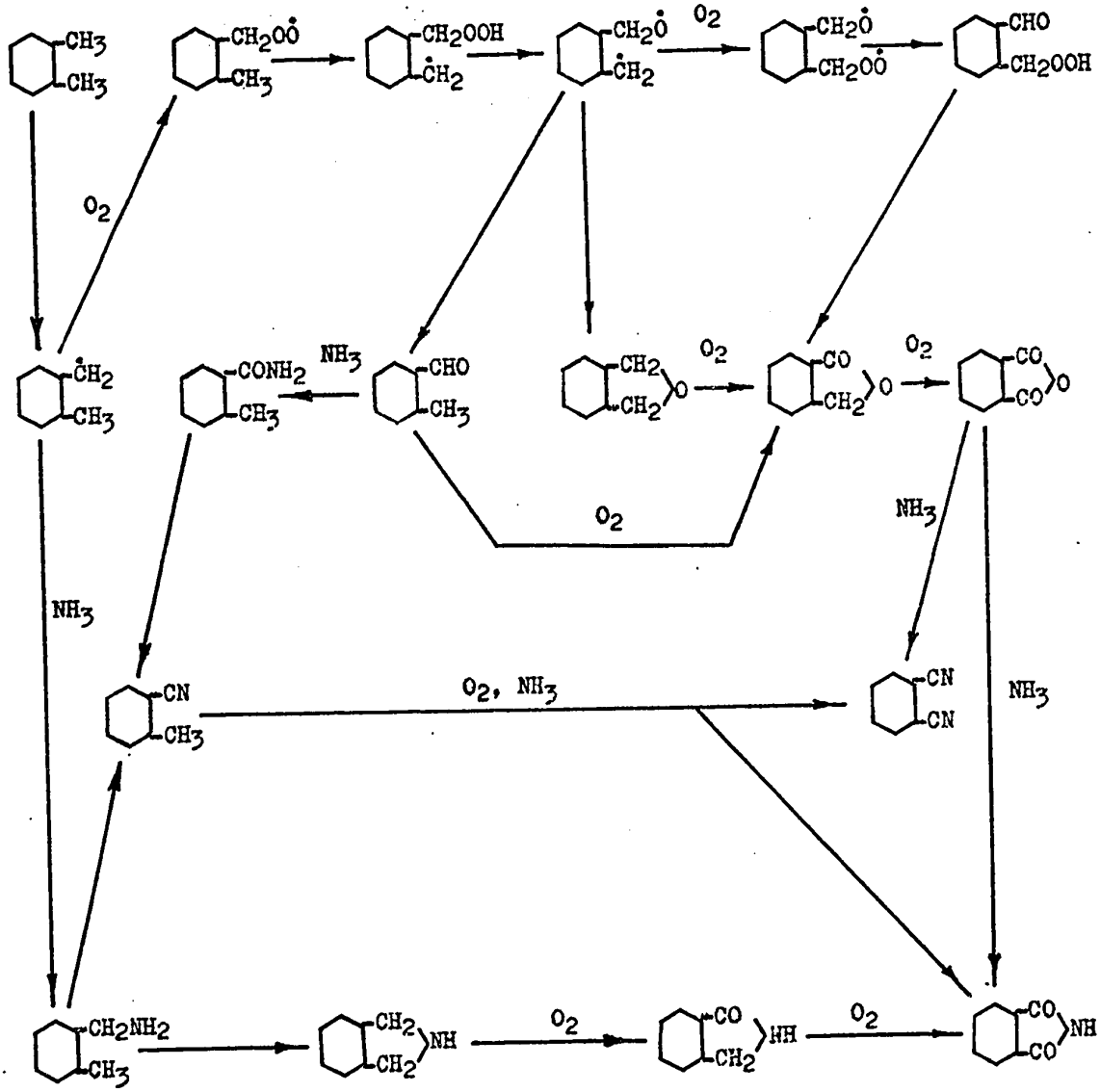
R Rate of formation

The subscripts X, T, P, and D are xylene, tolunitrile, phthalonitrile (and phthalimide), and carbon oxides and hydrogen cyanide, respectively.

Suvorov considered that the catalytic vapor phase ammoxidation includes a combination of reactions involving oxidation, ammonolysis, dehydrogenation, and dehydration, accompanying the formation of oxygen and nitrogen containing compounds. The catalysts generate free radicals, and at the same time initiate the main step of the reaction. This occurs on the parts of the surface with active oxygen by means of dehydrogenation of the initial and intermediate compounds. The materials being oxidized obtain oxygen in the bulk phase and

also in the neighborhood of the catalyst through surface complexes with the mobile form of oxygen. By transferring hydrogen atoms, hydroxyl groups and NH_2 groups to the adsorbed free radicals, the catalyst also plays a part in terminating chains in the bulk phase.

The reaction scheme of ammoxidation of o-xylene suggested by Suvorov and his co-workers is as follow.



B. Catalysts for the Ammoxidation of Xylenes

The effectiveness of searches for active and selective catalysts is controlled by the level of our understanding of the mechanisms. Referring to the above mentioned mechanisms the most acceptable concepts appear to be those which take into account the electronic properties of the catalyst surface. Another valid position appears to be the assumption that the surfaces take part in the radical chain reaction.

Vanadium oxide catalysts are the most widely used types for vapor-phase ammoxidation as well as oxidation. The oxide of molybdenum, tungsten, cobalt, manganese, copper, aluminum, niobium, tin, antimony, tantalum, silver, chromium, titanium, bismuth, iron and a number of other metals are also catalytically active to one extent or another in partial oxidation reactions of organic materials. They are usually used in mixtures of one with several others, or with vanadium oxide (3, 44). For the ammoxidation of xylenes the vanadium oxide and vanadium oxide based catalysts are commonly used. Recently a lot of workers have attempted to find out some non-vanadium catalysts. All the compounds tested are oxides of transition metals, that is, they are able to exist in at least several oxide forms. A list of catalysts used in ammoxidation reactions is given in Appendix I, Table 5.

III EXPERIMENTAL EQUIPMENT

The equipment was contructed by Rao (35) and was improved by Preudhomme (33) for qualitative studies of either vapor phase air oxidation or vapor phase ammoxidation with air-ammonia mixture as the oxidizing agent. For the purpose of quantitative studies the equipment had to be improved both with respect to the reactor system and analytical methods. This was done by the author in the manner described in this chapter.

The description of the experimental set up and the major individual units of the system is given below. The specifications of all other equipment are given in Appendix VI.

A. Flow Diagram

The experimental set-up consisted of three systems, which are:feeding system, reaction system and cooling system, and various temperature, pressure,flow measurement and heating devices. The details of the flow system are given in Figure 1.

1. Feeding system

Compressed air at 90-100 psig from the laboratory compressed air line was passed through an air filter with a stone filter screen in order to remove oil or dirt from the air. The clean air was passed through a dryer containing silica gel to keep the vapor content nearly the same. The air was then passed through a low pressure regulator(PR1) to reduce it to the required range of 7-9 psig. Then the air was passed through a rotameter (R1), (Tube No. B 344 or C 312), where the flow rate was monitored. The flow rate was

controlled by a needle valve (NV 1). The air was divided into two parts controlled by needle valves (NV 2 and NV 4). The main part was heated to about 270° C. in an electrical preheater prior to entering the carburettor. The other part was passed through the xylene feeding system. In that system o-xylene was kept at constant temperature (85° C.) with an automatic thermoset and the air was bubbled through the o-xylene. The flow rate was controlled by a needle valve (NV 4) and measured by a rotameter (R2), (Tube No. A 964). After that the two parts of air were mixed together and sent to the carburettor. The ammonia was passed from the tank into the carburettor through a low pressure regulator (PR 2) to reduce the pressure to the required range of 7-9 psig. The ammonia flow rate was measured by a rotameter (R3), (Tube No. 1/8 -15-G-5 and 3/32-06-p-5) and controlled by a needle valve (NV 3).

2. Reaction system

The carburettor and the reactor are included in this system. The carburettor, an electrically heated cylindrical vessel packed with one quarter inch berl saddles served two purposes. It thoroughly mixed the reactants, and it also brought them to a higher temperature. The mixture then entered the integral reactor. The reactor was heated by three independent electrical heaters, and had three distinct zones:

(1) preheating zone

(2) reaction zone

(3) buffer zone

The preheating zone and the buffer zone were packed with one quarter inch berl saddles, and the reaction zone was packed with the catalyst. The

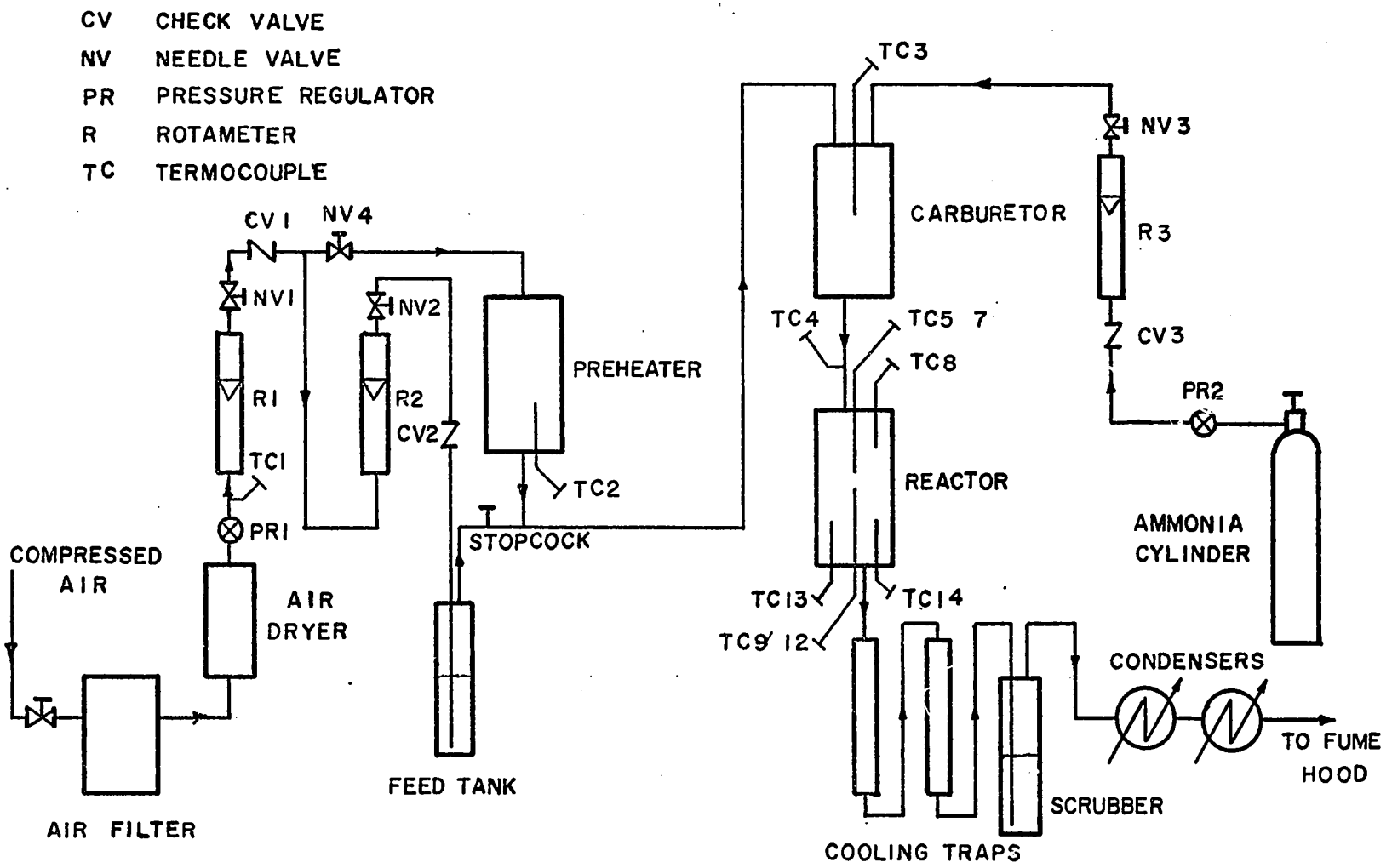


FIG. I. SCHEMATIC DIAGRAM OF THE EXPERIMENTAL APPARATUS

preheating zone was used to bring the mixture up to the desired reaction temperature. The reaction is highly exothermic, and the external heat supplied to the reactor had to be reduced in order to maintain isothermal conditions across the reaction zone. Due to the heat losses at the end of the reactor, that zone exhibited large temperature fluctuations and uneven temperature distribution. The buffer zone of berl saddles served to reduce uneven temperatures at the reactor end.

3. Cooling system

This system included two cooling traps, one scrubber and two water-cooled condensers.

The ammoxidation products were condensed in this system. The solid products, phthalonitrile and phthalimide, were mainly condensed in the first trap. Some of the tolunitrile was obtained in the second trap. The o-xylene and the tolunitrile were extracted in the scrubber filled with benzene. The benzene and the trace amount of o-xylene were cooled down by the water-cooled condensers.

The temperature was measured at fourteen different locations in the system as shown in Figure 1, by means of grounded and ungrounded chromel-alumel thermocouples (T1 - T14).

B. Details of Equipment

1. Reactor

The reactor was contructed from a 15½ inch section of 1 inch schedule 40, 304 stainless steel pipe. The ends of the pipe were welded to the slip-on flanges , and matching blind flanges completed the body of the reactor. The details of the reactor are shown in Figure 2. Asbestos gaskets,

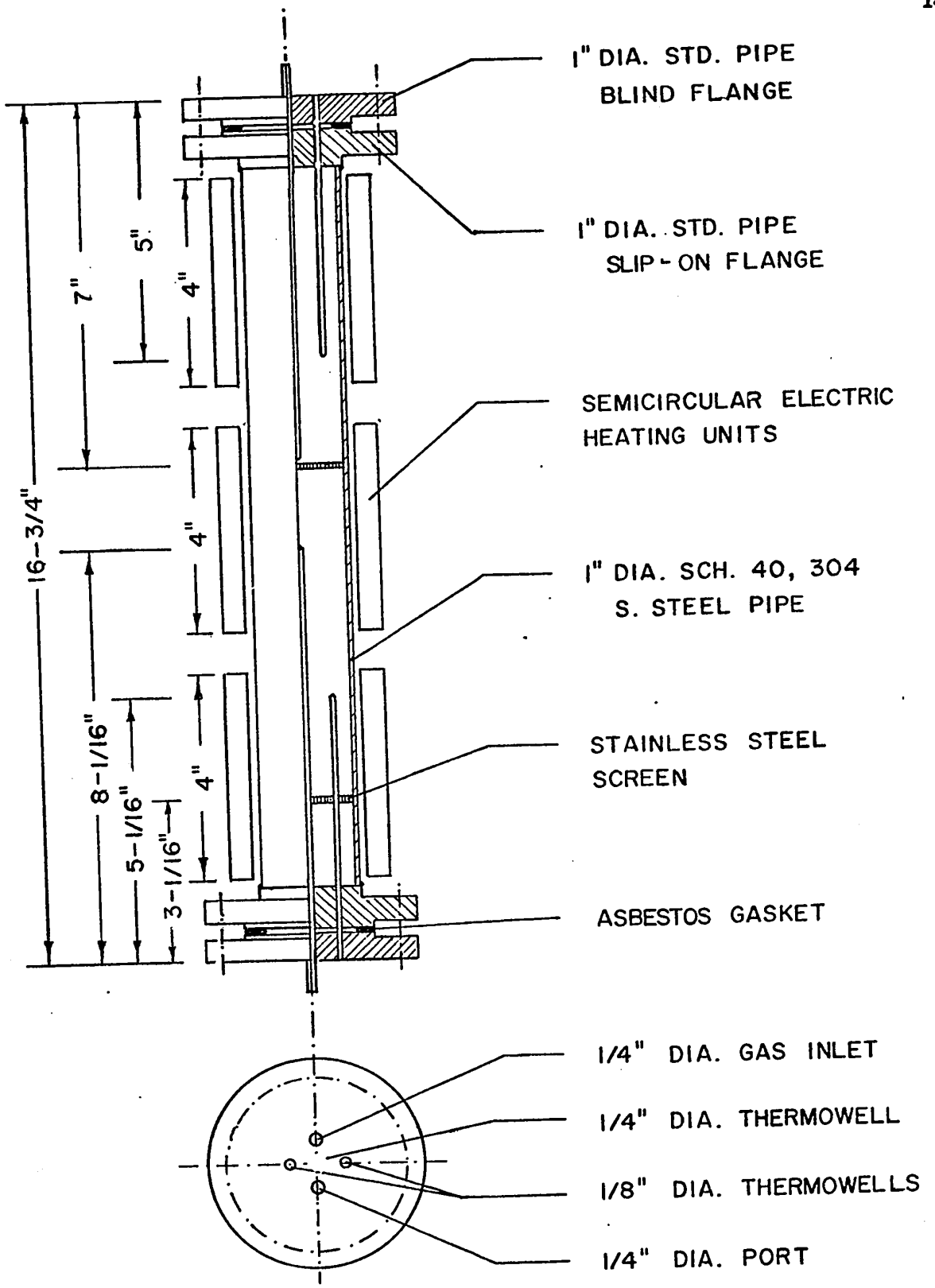


FIG. 2. SECTIONAL OF THE REACTOR

1/8 inch thick, 1 inch I. D. and 2 inch O. D. were used to obtain leakproof joints. A 1/8 inch O. D., 5 inch long stainless thermowell tube was welded to the top blind flange. Another 1/4 inch O. D., 7 inch long stainless steel thermowell tube was welded through the centre of the top blind flange. Two 1/4 inch stainless steel swagelok male connectors were inserted to the top flange to serve as the inlet to the reactor and to insert berl saddles into the reactor. Two 1/8 inch O. D., 5-1/16 inch long stainless steel thermowell tubes were welded to the bottom blind flange. A 1/4 inch O. D., 8-1/16 inch long stainless steel thermowell tube was welded through the centre of the bottom blind flange in order to allow four thermocouples to be inserted together. The reactor bed consisted of two stainless steel screens, 1/16 inch thick, which fitted tightly to the reactor tube.

The reactor was heated by three independently controlled semicylindrical heating units of 1½ inch I. D., 4 inch length, rated at 210 watts. The voltage applied to each heating element was controlled by means of a variable transformer. The reactor unit was insulated with glass wool and high temperature insulation.

2. Air Preheater

A sectional view of the preheater is shown in Figure 3. The preheater was constructed from an 18 inch section of 1-1/2 inch schedule 40, 304 stainless steel pipe. The ends of the pipe were welded to 300 psig welding neck flanges, and matching blind flanges. Two 1/8 inch O. D., 4 inch long stainless steel thermowell tubes were welded to both the top and bottom blind flanges. The preheater was completely packed with 1/4 inch berl saddles and was heated by two 12 inches long semicylindrical heating units, connected in parallel. Each of these units was rated at 700

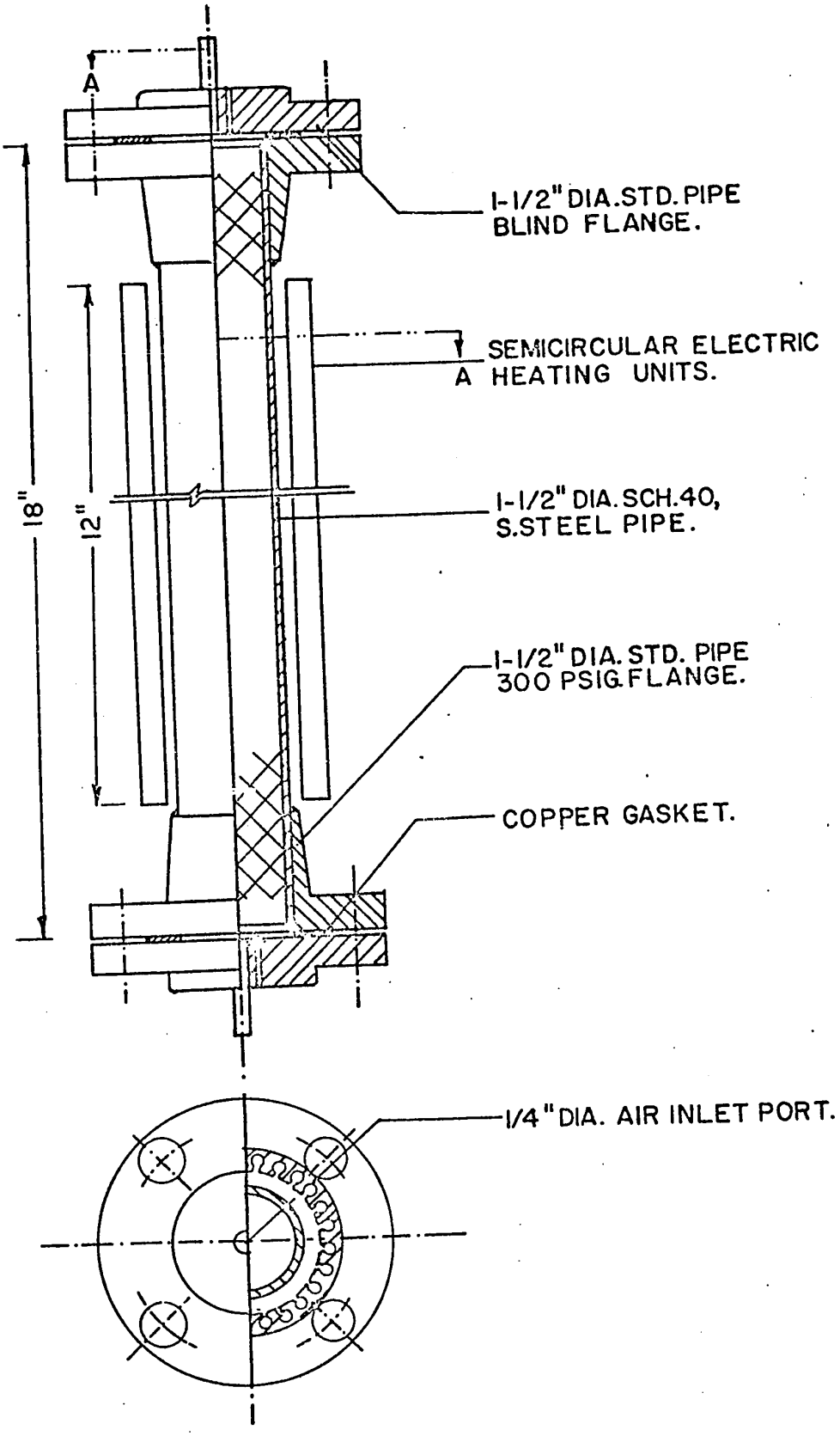


FIG.3 SECTIONAL VIEW OF THE PREHEATER.

watts and the power input was controlled by a variable transformer. The air preheater was insulated with glass wool.

3. Carburettor

The carburetor was constructed from an 11 inch long, 2 inch O.D. schedule 40, 304 stainless steel pipe (Figure 4).The top end was welded to a 2 inch, 150 psig standard pipe flange, and closed with a matching blind flange. A 1/4 inch stainless steel swagelok male connector was inserted through the centre of the top blind flange in order to put in a 1/8 inch O. D. stainless steel thermowell tube. Three stainless steel 1/4 inch swagelok male connectors were inserted in the blind flange to serve as inlet ports for the reactants. A 1/8 inch thick, 2 inch I. D., 4 inch O. D. aluminum gasket was used to give a leakproof joint. The bottom end was closed by welding on a 3 inch diameter, 1/2 inch thick steel plate. A 1/4 inch stainless steel swagelok male connector was inserted through the centre of the bottom to serve as an exit port for the preheated and mixed reactants. The carburettor was fully filled with 1/4 inch berl saddles to promote mixing, and was heated by two 8 inch long semicylindrical heating units connected in parallel. Each of the units was rated at 500 watts and the power input was controlled by a variable transformer. The carburettor was completely insulated with glass wool and high temperature insulation.

C. Analytical Method

The products were analysed using a Varian Aerograph Series 1520, dual column gas chromatograph. The sensing element used was a thermal conductivity detector. The signals from the thermal conductivity detector were recorded on a Varian Aerograph medel 30 strip chart recorder.

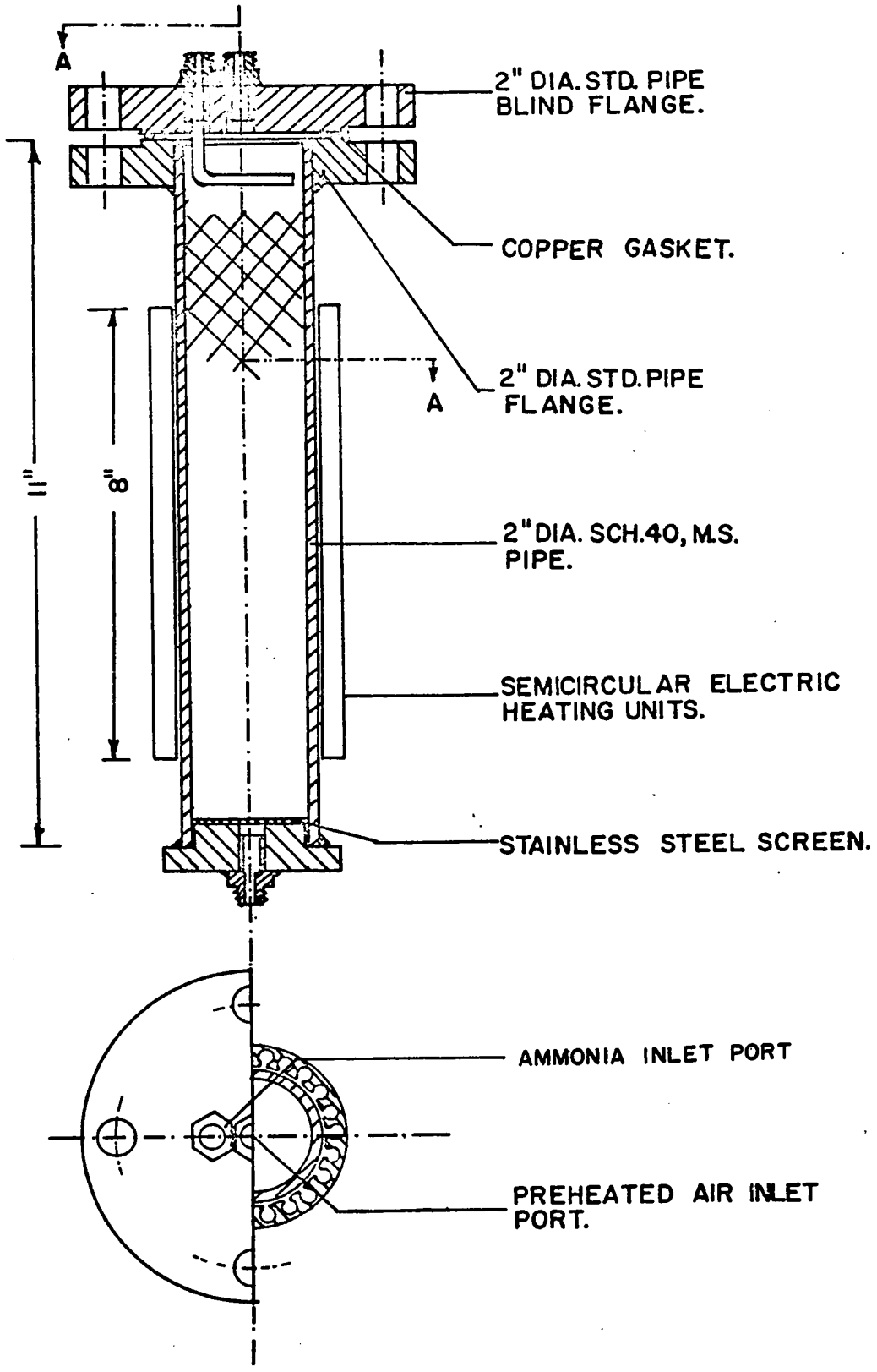


FIG.4 SECTIONAL VIEW OF THE CARBURETOR.

There was no standard method available in the literature for analysis of the products. The techniques used finally were developed through a lot of trials. Two columns were found which would seperate the products. The first of these two columns was a 10 foot by 1/8 inch stainless steel column packed with 8 % F. F. A. P. on 60/70 mesh acid washed, dimethyl-chloro-silane treated chromosorb W. This column showed good seperation of o-xylene, tolunitrile and phthalonitrile. The second column was a 6 foot by 1/8 inch stainless steel column packed with 3 % Neopentyl-glycol Succinate and 1 % ortho phosphoric acid (H_3PO_4) on 60/80 mesh chromosorb W. This column showed good seperation of phthalonitrile and phthalimide. All columns were supplied by The Chromatographic Specialities Ltd.

After a lot of trials the following analytical method was found to give good results. The products were dissolved in a mixed solvent of acetone and benzene. Pseudocumene and o-toluamide were added as internal standard. The F. F. A. P. column and a programing method, shown in Figure 5, were used. The flow rates of carrier gas for the column and the reference were 30 cc/min. and 330 cc/min. respectively.

D. Raw Materials

o-Xylene used in the experiments was highest purity supplied by Fisher Scientific Company, (product of Eastman Kodak Company). Acetone, Laboratory grade, and benzene, crystallizable, Fisher Certified ACS, were supplied by Fisher Scientific Company. Phthalonitrile, phthalimide, o-tolunitrile and o-toluamide used for calibration purposes were of Fisher's highest purity grade. Pseudocumene used in the analysis was the certified grade from the Aldrich Chemical Company, Inc., Milwaukee, Wisconsin.

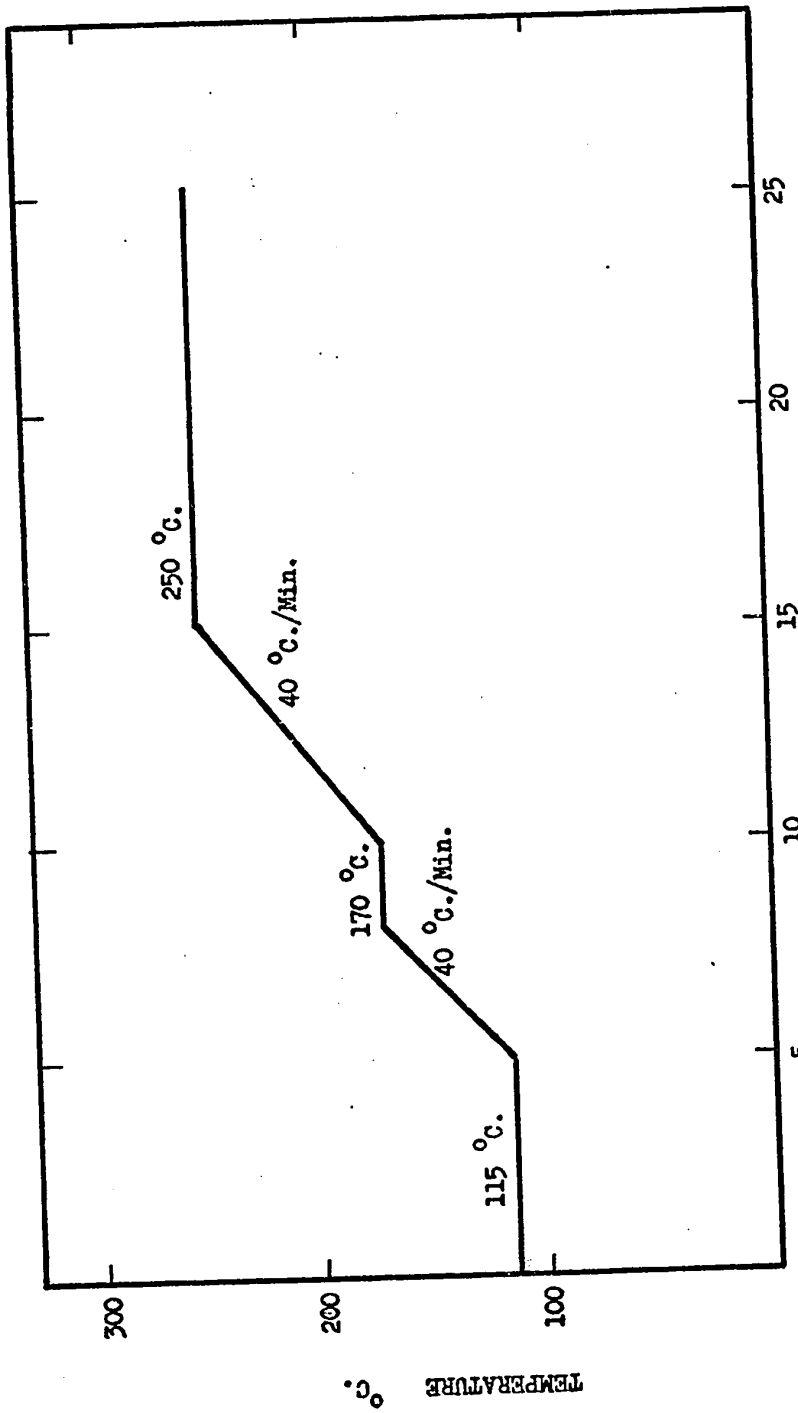


FIGURE 5 TIME VS. TEMPERATURE PROGRAM FOR GAS CHROMATOGRAPHY

E. Catalysts

A number of catalyst were tried. Some of them were supplied by M/S Harshaw Chemical Company, Cleveland, Ohio, U. S. A. and the others were made in the laboratory.

(1) Vanadia Catalyst (V-1002E)

This catalyst was supplied by Harshaw Chemical Company. The catalyst had a low surface area to mass ratio, and was chosen because this type of catalyst had previously been used succesfully for the vapor phase oxidation. The physical properties of the catalyst are given in Table 1, in Appendix I.

(2) $Sn(VO_3)_4$ Catalyst

This catalyst was prepared as follows. 11.6 grams $SnCl_4$ and 50 cc distilled water were added to 206 grams of alundum (1/8 inch sphere), 20.8 grams of ammonium vanadate suspended in 100 cc distilled water were added with stirring. The impregnated carriers, evaporated slowly at nearly 100° C., were then dried at 80° C. and calcinated in air at 500° C. for 4 hours.

(3) V_2O_5-K_2SO_4 Catalyst with Alundum Carrier

The preparation of this catalyst is detailed below.

210 grams alundum (1/8 inch sphere) were impregnated with a solution prepared from 15.8 grams ammonium vanadate, 42.6 grams of oxalic acid, 80 cc distilled water and 23.6 grams potassium sulphate. The impregnated carriers, evaporated at nearly 100° C., were dried at 80° C. and calcinated in air at 500° C. for 4 hours.

(4) V_2O_5 - K_2SO_4 Catalyst with preheated Alundum Carrier

The alundum of 1/8 inch sphere was preheated at 1200° C, for 24 hours. 6 grams vanadium pentoxide was suspended in 40 cc distilled water. The suspension was heated to 90 °C. and 21 grams oxalic acid were gradually added until the vanadium pentoxide was completely reduced and dissolved to give a blue solution of vanadyl oxalate. Then potassium sulphate was added and dissolved in the solution. This solution was poured over the preheated alundum (102 grams) and then evaporated to dryness at about 100 °C. with frequent stitting. The product was heated in a stream of air at 380 °C. for 16 hours to oxidise the vanadyl oxalate to vanadium oxide.

(5) V_2O_5 - K_2SO_4 Catalyst with preheated Activated Alumina Carrier

The activated alumina used was preheated at 900 °C. for 24 hours and then screened to 8 - 10 mesh. The procedure was the same as catalyst (4) except for the carrier used.

(6) Tungstate Catalyst

Four solutions were made seperately as detailed below.

Solution (a): 134 grams of $3(NH_4)_2O \cdot 7WO_3 \cdot 6H_2O$ was added to 1800 cc distilled water at 80° C.

Solution (b): 75.5 grams 50 % solution of $Mn(NO_3)_2$ was added to 200 cc distilled water.

Solution (c): 15.2 grams of $Co(CH_3COO)_2 \cdot 4H_2O$ was added to 300 cc distilled water at 85° C. with stirring.

Solution (d): 11.9 grams of K_2CrO_4 was added to 50 cc distilled water.

Solution (b) was added dropwise to solution (a) at 80° C. with stirring. The yellowish white precipitate, $3MnO \cdot 7WO_3 \cdot 11H_2O$, produced was washed throughly with water by decantation three times. Solution (d) was added to solution (c) dropwise at 85° C. with stirring for 30 minutes. The brown precipitate produced was washed by decantation for four times.

The above two precipitates were mixed with stirring and filtered. The filtered cake was dried at 50° C. for 16 hours. Then it was crushed and screened to 6 - 10 mesh.

IV EXPERIMENTAL PROCEDURE

A. Calibration Procedure

1. Calibration of the Air Rotameter

The two air rotameters were calibrated directly by using a wet test gas meter, supplied by the precision Scientific Company. Inlet pressure and temperature conditions were used for this calibration. The volumetric flow rate at the conditions of calibration were then converted to standard conditions (1 atm., $0^{\circ}C.$) so that this 'standard curve' could be used to determine the flow rates for the various inlet conditions. Since the major components of air (N_2, O_2) are practically insoluble in water, the presaturator of the wet test meter was filled with distilled water. The calibration curves are given in Appendix IV, Figure 9 and 10.

2. Calibration of the Ammonia Rotameter

The ammonia rotameters could not be directly calibrated using the wet test meter, because ammonia is highly soluble in water. The indirect calibration was carried out as follows. The rotameter was first directly calibrated using nitrogen gas and the precision wet test meter. The inlet pressure and temperature were used for this calibration. The flow rate was then converted to standard conditions (1 atm., $0^{\circ}C.$). Since the properties of the nitrogen and ammonia are quite different, the correction of the flow rate was done as follows.

$$W = Q = KD_f \sqrt{\frac{w_f(\rho_f - \rho)\rho}{\rho_f}}$$

$$\frac{W_a}{W_b} = \frac{K_a}{K_b}\sqrt{\frac{(\rho_f - \rho_a)\rho_a}{(\rho_f - \rho_b)\rho_b}} = \frac{Q_a\rho_a}{Q_b\rho_b}$$

Let a = NH_3 , b = N_2 , we get

$$Q_{NH_3} = \frac{K_a}{K_b}\sqrt{\frac{(\rho_f - \rho_a)}{(\rho_f - \rho_b)}}\cdot\sqrt{\frac{\rho_b}{\rho_a}}\ Q_{N_2}$$

Assume

$$\frac{K_a}{K_b}\sqrt{\frac{(\rho_f - \rho_a)}{(\rho_f - \rho_b)}} \approx 1$$

$$Q_{NH_3} = \sqrt{\frac{\rho_b}{\rho_a}}\ Q_{N_2} = 1.283\ Q_{N_2} \qquad (\text{at } 0^{\circ}C.,\ 1 \text{ atm.})$$

So that the flow rate of ammonia at standard conditions was computed using the above relationship. Ammonia was then run through the rotameter and dissolved in a known amount of standard HCl solution for a specific time. The solution was then titrated against a standard solution of sodium hydroxide, and the ammonia flow rate was computed . The experimental value of the ammonia flow rate agreed with the computed value to within ± 5 %. The calibration curves are given in Appendix IV, Figure 11 and 12.

3. Calibration of Thermocouples

The chromel-alumel thermocouples used were of grounded and ungrounded type. The ungrounded thermocouples were used in the preheater, carburetor and reactor because the A. C. current employed by the electrical heaters causes an induced e. m. f. (up to 2 mv) to accumulate in the system. If grounded thermocouples are used, the induced e. m. f. can result in inaccurate temperature measurement. The grounded thermocouples were used in the other places. The accuracy of the thermocouples was checked against a reference chromel-

alumel thermocouple, which was checked against the melting point of pure tin and zinc. All the thermocouples were accurate to ± 1°C.

B. Experimental Procedure

The reactor was charged with the required amount of catalyst, and then air from the compressed air line was turned on and controlled by the fine needle control valve at the outlet of the rotameter to obtain the desired flow rate. The heaters for the reactor, carburettor and air-preheater were then turned on gradually to reach the required temperatures. The heater of the xylene feeding system's oil bath was turned on and allowed to reach a steady temperature. The system took approximately 4 hrs.to reach steady state at 445° C. The ammonia and xylene were fed simultaneously to the carburettor. The flow rate of ammonia was controlled by the needle control valve at the outlet of the rotameter to obtain the required flow rate. The feeding rate of o-xylene was controlled by the flow rate of air, which was controlled by a needle valve at the outlet of the small air rotameter. Before the o-xylene and ammonia were added to the reactor, the heat supply to the reactor had to be lowered by adjusting the variable transformers because of the exothermal nature of the reaction. Once the desired flow rates of air, ammonia and o-xylene had been established, the system was allowed to run for approximately one hour so that a position of dynamic equilibrium and isothermal conditions could be reached. At this point the sampling of feeding system and cooling system were begun and contiued for one hour. Over the duration of the run, the reactor temperatures were frequently checked. At

the end of the run the products in the cooling system were dissolved in acetone and benzene for subsequent analysis. The flow rate of o-xylene was calculated by the weight difference of o-xylene feeding tank between the end and beginning. At the end of a day's operation, nitrogen was passed through the system for about 30 min. The flows of ammonia and o-xylene were shut off. The air flow was allowed to continue until the system was back to room temperature.

V EXPERIMENTAL RESULTS

A. Screening of Catalysts

Six catalysts with compositions, shown in Chapter III, were tried. The results are detailed below.

1. Catalysts (1) to (4), Vanadia, $Sn(VO_3)_4$, V_2O_5 - K_2SO_4 on alundum untreated and treated.

Some yellow brown solid was observed in the cooling trap. A lot of liquid product was obtained in two layers. The products were analyzed by gas chromatography. The products were unreacted o-xylene and o-tolunitrile.

2. V_2O_5 - K_2SO_4 catalyst with preheated activated alumina

The experiments were carried out at 280 - 340 °C. A lot of solid product was obtained. It was analyzed by gas chromatography and identified by infra-red to be a mixture of phthalonitrile and phthalimide, the main part being phthalimide. The liquid part was unreacted o-xylene and o-tolunitrile. This agrees with Ohara's result (32), that the phthalimide is formed as principal product.

After thirty runs the catalyst was damaged. It seemed that the catalyst was not stable. Ohara in his studies suggests that vanadium oxide is very active for oxidation of ammonia. This is a very exothermic reaction and tends to reduce the selectivity of the catalyst. As a result of the catalyst deactivation observed, this catalyst was not considered to be a suitable catalyst for producing phthalonitrile.

3. $3MnO \cdot 7WO_3 \cdot 11H_2O$ - $CoCrO_4 \cdot 2H_2O$ Catalyst

The experiments were conducted at 400 - 455° C. A lot of solid product was obtained. It was phthalonitrile and phthalimide. The yields were higher than for catalyst (5) and phthalonitrile was the main product. The liquid product obtained was o-xylene and o-tolunitrile.

Based on the rather rough screening procedure outlined above, it appeared that tungstate catalyst should be attractive for the ammoxidation of o-xylene. It was therefore decided to carry out futher experimentation using this catalyst.

B. The effects of the main reaction parameters

1. Reaction Temperature

The results are shown in Figure 6. and Table 1. It is seen that the total conversion of o-xylene is increased by increasing the temperature and the formations of phthalonitrile and phthalimide is also increased.

2. Concentration of Ammonia

The results are shown in Figure 7. and Table 2. It is seen that for mole ratio of ammonia to o-xylene greater than 4, the rates of formation are constant. This result is similar to that found by Ito for the ammoxidation of o-xylene over a vanadium catalyst (14).

3. Contact Time

Contact times were varied between 0.8 and 7 seconds. The results are shown in Figure 8 and Table 3. The total conversion of o-xylene and the conversion to carbon oxides and hydrogen cyanide increased with increasing contact time. The conversions to o-tolunitrile, phthalonitrile and phthalimide first increase and then decrease with the contact time.

CATALYST : 55 CC

CONC. OF o-XYLENE : 0.65 %

CONC. OF AMMONIA : 4.0 %

CONTACT TIME : 2 SECONDS

○ o-XYLENE ● PHTHALONITRILE

△ o-PHTHALIMIDE ▲ o-TOLUNITRILE

■ CO_2,,CO, HCN

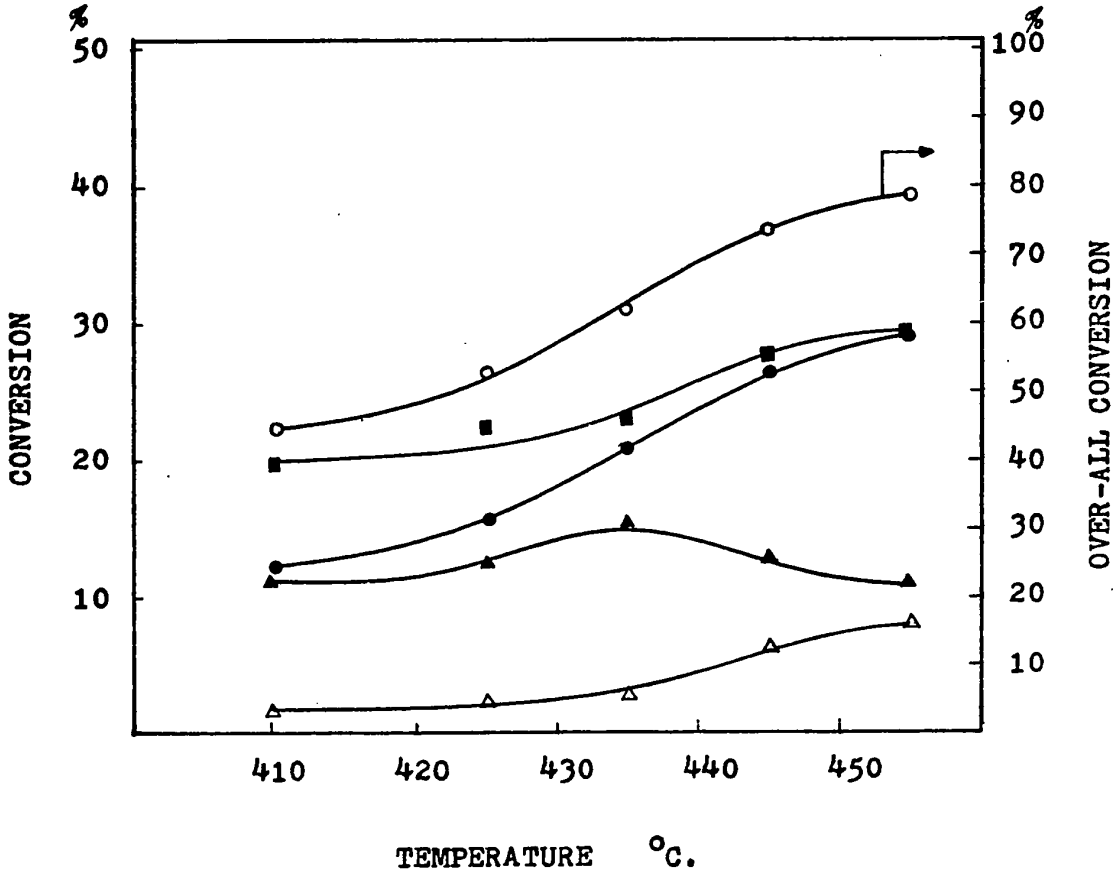


FIGURE 6. EFFECT OF TEMPERATURE

CATALYST	:	55 CC
REACTION TEMPERATURE	:	445 °C.
CONC. OF o-XYLENE	:	0.65 %
CONTACT TIME	:	2 SECONDS

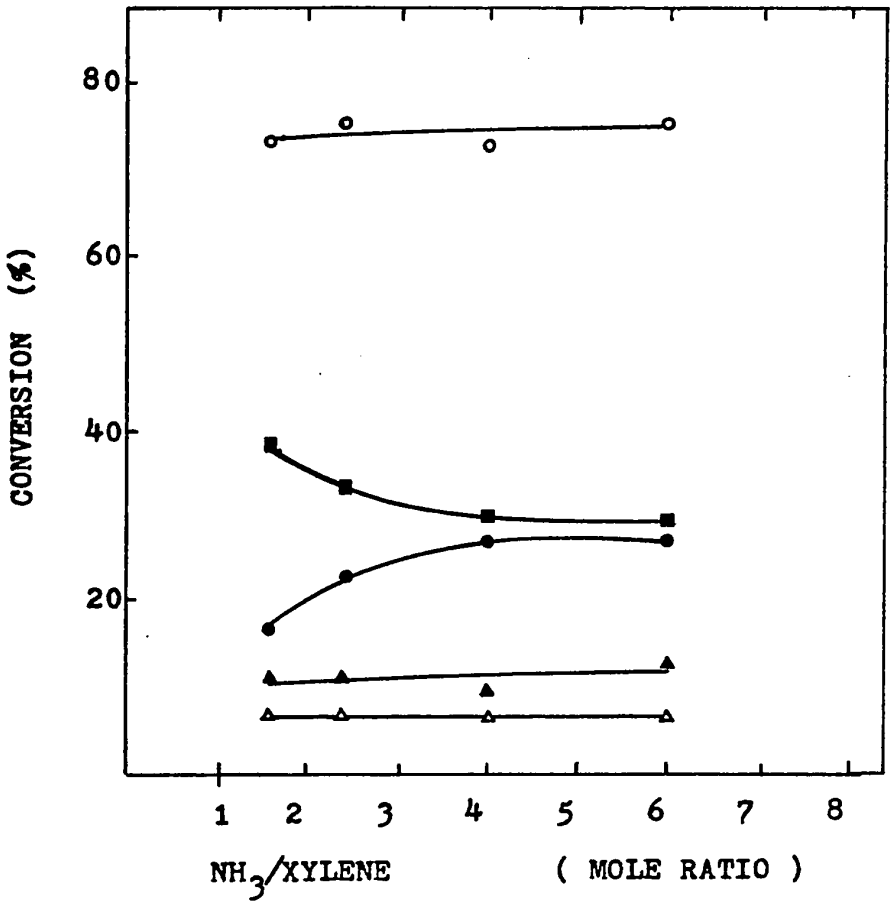


FIGURE 7. EFFECT OF AMMONIA/o-XYLENE

○	o-XYLENE	●	PHTHALONITRILE
△	o-PHTHALIMIDE	▲	o-TOLUNITRILE
■	CO_2, CO, HCN		

CATALYST	:	55 CC
REACTION TEMPERATURE	:	445 °C.
CONC. OF o-XYLENE	:	0.65 %
AMMONIA/XYLENE (MOLE RATIO)	:	6

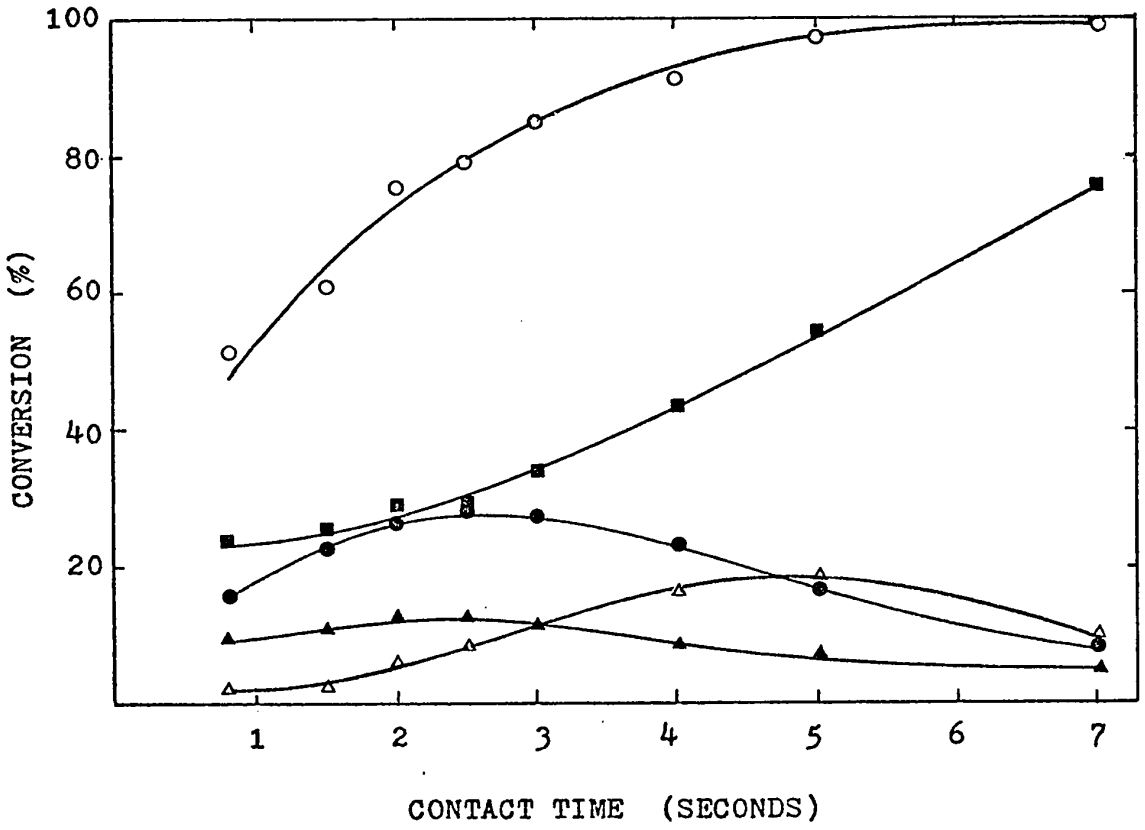


FIGURE 8. EFFECT OF CONTACT TIME

○ o-XYLENE	● PHTHALONITRILE
△ o-PHTHALIMIDE	▲ o-TOLUNITRILE
■ CO_2, CO, HCN	

TABLE 1. EFFECT OF TEMPERATURE

Catalyst 55 cc

Conc. of o-Xylene 0.65 %

Conc. of Ammonia 4.0 %

Contact Time 2 seconds

Temperature (°C.)	Conversion of o-Xylene (%)	Conversion to (%) TN	PN	PI	CO_2, CO HCN
410	44.56	11.33	12.40	1.75	19.08
425	52.63	12.38	15.45	2.22	22.58
435	61.99	15.54	20.76	2.64	23.05
445	73.79	12.85	26.37	6.18	28.39
455	78.08	11.24	29.24	8.03	29.50

TABLE 2. EFFECT OF AMMONIA/o-XYLENE

Catalyst 55 cc

Temperature 445 °C.

Conc. of o-Xylene 0.65 %

Cantact Time 2 seconds

NH_3/Xylene Mole Ratio	Conversion of o-Xylene (%)	Conversion to (%) TN	PN	PI	CO_2,CO HCN
1.6	73.54	11.56	16.53	6.74	38.71
2.4	75.45	11.21	23.56	6.97	33.71
4.0	73.06	9.93	26.76	6.24	30.03
6.0	75.52	12.80	26.90	6.32	29.50

TABLE 3. EFFECT OF CONTACT TIME

Catalyst 55 cc

Reaction Temperature 445 °C.

Conc. of o-Xylene 0.65 %

NH_3/o-Xylene (Mole Ratio) 6

Contact Time (sec.)	P_{XO} atm (10^{-3})	Conversion of o-Xylene (%)	Conversion to (%) TN	PN	PI	CO_2,CO HCN
7.0	7.6	100.00	5.10	8.76	10.33	75.81
5.0	6.5	97.42	7.04	17.09	18.86	54.43
4.0	6.7	91.30	8.47	23.04	16.28	43.51
3.0	6.3	85.16	11.83	27.34	11.72	34.27
2.5	6.5	79.25	12.66	28.65	8.33	29.61
2.0	6.1	75.52	12.80	26.90	6.32	29.50
1.5	6.3	60.70	10.09	22.37	2.39	25.85
0.8	6.3	51.28	9.63	15.24	2.30	24.11

VI DISCUSSION OF RESULTS

A. The Choice of the Catalyst

In this investigation, six catalysts were tried in the laboratory and it was found that the vanadium oxide is not as suitable for this ammoxidation as some of the other catalysts tried. Vanadium oxide is able to catal yze the oxidation of ammonia to nitric oxide, nitro-compounds may also appear as intermediate products in the ammoxidation of o-xylene. A reddish-brown gas was indeed found in ammoxidation over a vanadium catalyst with excess ammonia. This agrees with Ohara's suggestion that the oxidation of ammonia tends to reduce the selectivity of vanadium catalyst (32).

Secondly, the experimental results showed that the carrier and the treating process of the carrier influence the catalytic effect. It was seen that the preheated activated alumina is more active than the inert alundum.

The tungstate catalyst showed the best results, although not as good as report in US Patent 3,312,710. The preparation process of catalyst must have some thing to do with its performance.

B. Performance Characteristics of Tungstate Catalyst

1. Effect of Temperature

As observed earlier, the total conversion of o-xylene is increased by an increase in temperature. From a yield point of view, it might be considered desirable to try higher temperatures, although consideration of selectivity and temperature run-away may ditate lower temperatures.

2. Effect of Ammonia/o-Xylene mole ratio

The results (Figure 7.) indicat that a mole ratio higher than 4 should be selected. Usually, a mole ratio of ammonia to o-xylene of 5 is preferable.

3. Effect of Contact Time

The effect of contact time is obvious. The total formation of CO_2, CO and HCN is highly affected by the contact time. The results show that a contact time of 2.0 - 2.5 seconds at a temperature range of 445 - 455 ^{o}C. is preferable for production of phthalonitrile, because side reactions are minimal for these conditions.

C. Quantitative Treatment of Kinetic Data

The estimation of the partial pressure at the surface of the catalyst particles is important for a catalytic vapor phase reaction. The ammoxidation of o-xylene is a very complex reaction. The mechanism is not clear. The physical properties of catalyst are also not well known, so that it was hard to estimate interfacial partial pressure precisely. Rough estimates were made following the approach of Yoshida (51). A typical value of the ratio of the pressure drop of o-xylene to the total pressure at the catalyst surface was found to be 0.0013 . In view of the small values for this ratio, it was considered safe to neglect interface mass transfer effects. The intraparticle diffusion effects were not estimated separately, and thus the rate constants deduced in this work should be considered as apparent rate con-

stants.

In reducing the rate data kinetically, it was considered proper to first try the reaction scheme suggested by Ito (15) for vanadium pentoxide catalyst. Ito's reaction scheme, shown in Chapter II, upon integration, leads to the following relationships :

$$P_{XO} \cdot Q_X = k_X \cdot R \cdot T \cdot t$$

$$Q_T = \frac{s}{1-r}\left\{ (1 - Q_X)^r - (1 - Q_X) \right\}$$

$$Q_P / Q_X = \frac{k_5}{k_X} - \frac{k_2 s}{k_X(1 - r)} \left[\frac{1}{r}\left\{ 1 - (1 - Q_X)^r \right\} - Q_X \right] \frac{1}{Q_X}$$

$$Q_D / Q_X = \frac{k_3}{k_X} - \frac{k_4 s}{k_X(1 - r)} \left[\frac{1}{r}\left\{ 1 - (1 - Q_X)^r \right\} - Q_X \right] \frac{1}{Q_X}$$

For the present data, $P_{XO} \cdot Q_X$ vs. contact time was not a linear plot. Ito's reaction scheme, therefore, does not fit the data satisfactorily.

The relationship between C_X and contact time t is as follows :

$$C_X = C_{XO}\, e^{-at}$$

where $a = 0.6858 \quad \text{sec.}^{-1}$

Treating experimental data by non-linear least square fitting, the variance of residuals with 7 degrees of freedom is 0.1869×10^{-16} and the data of C_X (observed and predicted) are shown in Table 7.1 (Appendix III).

From the above equation the over-all reaction rate of o-xylene is

$$R_X = -\frac{d\, C_X}{d\, t} = a\, C_{XO}\, e^{-at} = a\, C_X$$

The results show that the over-all reaction of o-xylene is of the first-

order.

Secondly, the reaction scheme was assumed as a consecutive- irreversible reaction

$$XY \xrightarrow{k_1 C_X} TN \xrightarrow{k_2 C_T} P \xrightarrow{k_3 C_P} D$$

where XY : o-xylene

TN : o-tolunitrile

P : phthalonitrile and phthalimide

D : CO_2, CO and HCN

The rate expressions for the various steps in the above scheme were found to be as follows :

$$R_X = -\frac{d C_X}{d t} = k_1 C_X$$

$$R_T = \frac{d C_T}{d t} = k_1 C_X - k_2 C_T$$

$$R_P = \frac{d C_P}{d t} = k_2 C_T - k_3 C_P$$

$$R_D = \frac{d C_D}{d t} = k_3 C_P$$

The system of linear equations was solved and the results were obtained as follows :

$$(1-Q_X) = e^{-k_1 t}$$

$$Q_T = \frac{k_1}{k_2 - k_1} e^{-k_1 t} + \frac{k_1}{k_1 - k_2} e^{-k_2 t}$$

$$Q_P = \frac{k_1 k_2}{(k_2 - k_1)(k_3 - k_1)} e^{-k_1 t} + \frac{k_1 k_2}{(k_1 - k_2)(k_3 - k_2)} e^{-k_2 t}$$

$$+ \frac{k_1 k_2}{(k_1 - k_3)(k_2 - k_3)} e^{-k_3 t}$$

$$Q_D = 1 - \frac{k_2 k_3}{(k_2 - k_1)(k_3 - k_1)} e^{-k_1 t} - \frac{k_1 k_3}{(k_1 - k_2)(k_3 - k_2)} e^{-k_2 t}$$

$$- \frac{k_1 k_2}{(k_1 - k_3)(k_2 - k_3)} e^{-k_3 t}$$

The data fitting in the above relationships were done by using a non-linear least square program, step by step. The results are shown below.

$k_1 = 0.6883 \quad \text{sec.}^{-1}$

$k_2 = 2.2748 \quad \text{sec.}^{-1}$

$k_3 = 1.376 \quad \text{sec.}^{-1}$

The variances of residuals with 7 degrees of freedom are 0.1619×10^{-2}, 0.3482×10^{-2} and 0.4487×10^{-1}, respectively. The data of ($1 - Q_X$), Q_T and Q_P (observed and predicted) are shown in Table 7.2 to 7.4 (Appendix III). The results showed that this reaction scheme does not fit.

Futher fitting of the data was done by the procedure outlined below.

(1) Establishing concentration - time relationships

The data were fitted to different equations using the non-linear least square method and the results are shown below.

(a) C_X vs. t

$$C_X = a\, e^{-bt}$$

where $a = 0.8381 \times 10^{-7}$ mole cc^{-1}

$b = 0.5437$ sec.^{-1}

The variance of residuals with 6 degrees of freedom is 0.8133×10^{-17} and the data of C_X (observed and predicted) are shown in Table 7.5 (Appendix III). The relationship is valid for the range of contact time of 0.8 to 7.0 seconds. The same restriction applies to the following data fitting.

(b) C_T vs. t

$$C_T = a\, e^{-(t-c)^2/b} \qquad (2)$$

where $a = 0.1325 \times 10^{-7}$ mole cc^{-1}

$b = 9.366$ $sec.^{-2}$

$c = 2.493$ sec.

The variance of residuals with 5 degrees of freedom is 0.9180×10^{-18} and the data of C_T (observed and predicted) are shown in Table 7.6 (Appendix III).

(c) C_P vs. t

$$C_P = a\, t^2 + b\, t + c \qquad (3)$$

Where $a = -0.2570 \times 10^{-8}$ mole cc^{-1} $sec.^{-2}$

$b = 0.2044 \times 10^{-7}$ mole cc^{-1} $sec.^{-1}$

$c = 0.4092 \times 10^{-8}$ mole cc^{-1}

The variance of residuals with 5 degrees of freedom is 0.6623×10^{-17} and the data of C_P (observed and predicted) are shown in Table 7.7 (Appendix III).

(d) C_D vs. t

$$C_D = a\, t \qquad (4)$$

where $a = 0.1335 \times 10^{-7}$ mole cc^{-1} $sec.^{-1}$

The variance of residuals with 7 degrees of freedom is 0.5600×10^{-16} and

the data of C_D (observed and predicted) are shown in Table 7.8 (Appendix III). The results are not so good especially at the contact time of 0.8 seconds. For the purpose of simplifying the calculations, equation (4) was chosen to fit the reaction schemes.

(2) Calculation of rates

From equations (1) to (4), the rates can be calculated corresponding to sixteen concentration levels as shown in Table 7.9 and 7.10. In Tables 7.11 to 7.14 that follow, RX OBS. and (RX-RT) OBS. are the values of the rates as calculated from equations (1) to (4).

(3) Fitting the rate data to different reaction schemes

(a) $$XY \xrightarrow{k_1 C_X^{k_2}} TN \xrightarrow{k_3 C_T^{k_4}} P \xrightarrow{k_5 C_P^{k_6}} D$$

$$R_X = k_1 C_X^{k_2}$$

where $k_1 = 0.5437157 \quad \text{sec.}^{-1}$

$$k_2 = 1.0000002 \approx 1$$

The results showed that the over-all reaction of o-xylene is of first-order. From the point of view of first-order reaction, this can be derived directly from equation (1).

$$R_X = 0.5437\ C_X$$

The variance of residuals with 14 degrees of freedom is 0.45909×10^{-25} and the data of R_X (observed and predicted) are shown in Table 7.11 (Appendix III).

$$R_T = k_1 C_X^{k_2} - k_3 C_T^{k_4}$$

$$R_X - R_T = k_3 C_T^{k_4}$$

where $k_3 = 0.01477 \quad sec.^{-1}$

$k_4 = 0.7610$

The variance of residuals with 14 degrees of freedom is 0.25764×10^{-16} and the data of $((R_X - R_T)$ (observed and predicted) are shown in Table 7.12 (Appendix III).

$$R_D = k_5 C_P^{k_6}$$

where $k_5 = 0.133498 \times 10^{-7} \quad sec.^{-1}$

$k_6 = -0.640916 \times 10^{-6}$

so that $R_D = 0.1335 \times 10^{-7}$

From the point of view of zero-order reaction, this can be derived directly from equation (4).

(b)

$$XY \xrightarrow{k_1 C_X} TN \xrightarrow{\frac{k_2 C_T}{1 + k_3 C_T}} P \xrightarrow{k_4} D$$

$$R_X = k_1 C_X$$

$$R_T = k_1 C_X - \frac{k_2 C_T}{1 + k_3 C_T}$$

$$R_P = \frac{k_2 C_T}{1 + k_3 C_T} - k_4$$

$$R_D = k_4$$

The values of k_1 and k_4 are same as reaction scheme (a).

$$R_X - R_T = \frac{k_2 C_T}{1 + k_3 C_T}$$

where $k_2 = 1.8421 \quad sec.^{-1}$

$$k_3 = 4.9804 \times 10^{8} \quad \text{mole}^{-1}\ \text{cc}$$

The variance of residuals with 14 degrees of freedom is 0.25326×10^{-16} and the data of ($R_X - R_T$) (observed and predicted) are shown in Table 7.13 (Appendix III). The results were poor.

(c)

$$XY \xrightarrow{k_1 C_X} TN \xrightarrow{\frac{k_2 C_T}{1 + k_3 C_X}} P \xrightarrow{k_4} D$$

The k_1 and k_4 are same as reaction scheme (a).

$$R_X - R_T = \frac{k_2 C_T}{1 + k_3 C_X}$$

where $k_2 = 0.69503 \quad \text{sec.}^{-1}$

$$k_3 = -0.13696 \times 10^{-8} \quad \text{mole}^{-1}\ \text{cc}$$

The variance of residuals with 14 degrees of freedom is 0.16378×10^{-17} and the data of ($R_X - R_T$) (observed and predicted are shown in Table 7. 14 (Appendix III). The results showed that for high concentration range of o-xylene(correspond to contact times 0.8 - 4 seconds) is quite good, but the value of k_3 is negative which is hard to explain.

Six more postulated reaction schemes were tested for their fit. None of the scheme that were tried seemed to give a totally satisfactory fit. From the schemes tested, (c) appears to be most promising scheme for the 0.8 - 4.0 seconds contact time. The actual reaction kinetic is in all probability more complex than the models that have been tried. One difficult in proposing more complex kinetic schemes is the limitation imposed by the data themselves, in that it is difficult to justify evaluation of too many constants from only eight experimental runs.

D. Comparision with Previous Work

Ito (14) investigated this ammoxidation reaction over a vanadium catalyst. The range of temperature for Ito's investigation is higher than that used in this present work. The general trends observed are nonetheless quite similar. The effect of ammonia/o-xylene mole ratio is also similar for the two investigation. The effect of contact time was studied by Ito at 470 ^{o}C., as compared to 445 ^{o}C. for the present work. Ito observed no maxima for the phthalonitrile or phthalimide formation, while the results for the tungstate catalyst show the definite maxima for both components. The trends for other components are, as expected, similar.

VII CONCLUSION

Of the six catalysts tried in th s investigation, tungstate catalyst seemed the most promising for o-xylene ammoxidation. The quantitative data obtained on this catalyst confirmed this promise. A good condition for production of phthalonitrile by ammoxidation of o-xylene would be as follows :

Temperature	:	445 - 455 °C.
NH_3/o-xylene (mole ratio):		5
Contact time	:	2.0 - 2.5 seconds

The quantitative treatment of data indicated that the reaction scheme is in all probability quite complex. Only a few of the possible schemes were looked into in the present investigation.

The over-all reaction of o-xylene is of first-order.

Quite apparently, considerable scope exists for further investigations on this reaction as well as related oxidation.

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APPENDIX I

THE CATALYSTS USED IN AMMOXIDATION

Table 4. Physical Properties of Vanadia Catalyst

Type	Vanadia oxidation catalyst V - 1002 E 3/16"
V_2O_5 Content	6 %
MoO_3 Content	3 %
Carier	Inert, alpha alumina
Apparent Bulk Density	83 lb./cu. ft.
Surface Area	1 m^2/gm
Size	3/16 in. spheres

Table 5. A List of Catalysts Used in Ammoxidation

Catalyst Composition	Raw Materials	References
V_2O_5	Xylenes	5, 6, 7, 14, 15, 16, 28, 39, 52
V_2O_5-K_2SO_4 (Al_2O_3)	o- and m-Xylene naphthalene	29, 30, 31
V_2O_5 - MoO_3(Al_2O_3)	Xylenes Gasoline	1, 12, 13, 22, 25, 26, 29
V - Sn	Xylenes Toluene Ethyl Benzene	19, 22, 23, 34, 43
V - Cr	m- and p-Xylene Toluene	17, 51
V_2O_5 - Sb_2O_3 (Al_2O_3)	m- and p-Xylene	4, 17
V - Mo - P	Xylenes Toluene Pseudocumene	2, 3, 9
V - Sn - P	Xylenes Toluene	41
V - Sn - Ti	Xylenes Terpenic Hydrocarbons	45
V_2O_5 - Li_2SO_4- H_2SO_4	m-Xylene	11
V_2O_5 - Na_2SO_4 - H_2SO_4	m-Xylene	10
V_2O_5 - MoO_3 - MnO_2 (Al_2O_3)	m- and p-Xylene	24
V - Cr - X (X=Mn, Pb, Mo, B or Co)	m-Xylene	46, 47, 48, 49, 50
MoO_3	m- and p-Xylene	7
Mo - X (X=Fe, Mn, Cr,Bi,Co, or Ni)	p-Xylene Hydrocarbons Gasoline	1, 22, 36, 37

Catalyst Composition	Raw Materials	References
Sn - Mo (or Bi)	Hydrocarbons	22
Fe - X (X=B, S, V, W, U, Pb or Sn)	p-Xylene	36
P - X (X=Fe, Ni, Co, Mn, or Cr)	p-Xylene	36
Fe - As	p-Xylene Propylene iso-Butene	27
$3MnO \cdot 7WO_3 \cdot 11H_2O$	Xylenes Toluene Pseudocumene Mesytilene	42

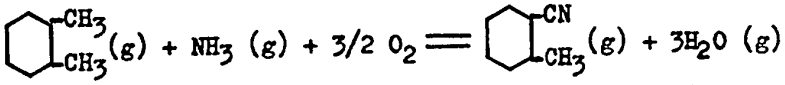
APPENDIX II

THERMODYNAMIC CALCULATIONS OF REACTIONS

THERMODYNAMIC CALCULATIONS

A. Derivation of the Heat Content Equation

For example, consider the following reaction:



The heat of reaction (H^o) at atmosphere and 298° K. is calculated as follows:

$$\Delta H^o = \Sigma \Delta H_f^o \text{ (Products)} - \Sigma \Delta H_f^o \text{ (Reactants)} \quad (1)$$

$$\Delta H^o = 43.72 + 3(-57.80) - 4.54 + (-11.04) + 3/2\ (0.0)$$

$$= -123.18 \text{ KCal/(g-mole)}$$

where H_f^o values were found from the 'Handbook of Chemistry and Physics' and estimated by Franklins Method (Refer to Reid, R. C. and Sherwood, T. K.; 'The Properties of Gases and Liquids').

Similarly, the heat capacity equation for this reaction is a function of temperature.

$$\Delta C_p = \Sigma C_p^o \text{ (Products)} - \Sigma C_p^o \text{ (Reactants)} \quad (2)$$

$$\Delta C_p = 10.272 - 21.4(10^{-3})T + 8.30(10^{-6})T^2 \quad (3)$$

Where C_p^o was estimated with Dobratz' Equation, which is

$$C_p^o = 4R + N_r'R/2 + Q_i C_{vi} + \frac{3N - 6 - N_r' - Q_i}{Q_i} Q_i C_{di} \quad (4)$$

The values of R, N_r', Q_i, C_{vi} and C_{di} were found in Perry's Chemical Engineer's Handbook (pp. 3 - 219).

At constant pressure,

$$\left(\frac{\partial H}{\partial T}\right)_p = C_p \quad (5)$$

and

$$\Delta H_{T_2} - \Delta H_{T_1} = \int_{T_1}^{T_2} C_p \, dT \qquad (6)$$

$$\Delta H_{298} - \Delta H_o^* = \int_0^{298} 10.272 - 21.4(10^{-3})T + 8.30(10^{-6})T^2 \, dT$$

where $\Delta H_o^* = -125{,}364$ Cal/(g - mole)

In general,

$$\Delta H_T - \Delta H_o^* = \int_0^T 10.272 - 21.4(10^{-3})T + 8.30(10^{-6})T^2 \, dT$$

$$\Delta H_T = -125{,}364 + 10.272\,T - 21.4(10^{-3})T^2/2 + 8.30(10^{-6})T^3/3 \qquad (7)$$

The heat of reaction at any temperature can be found from Equation (7). This equation will be valid within the range of the heat capacity Equation (3) and above the temperature of any phase transformation that may occur.

B. Derivation of Equilibrium Constants

The Van't Hoff Isobar is used as the starting point here,

$$\frac{d(\ln K)}{dT} = \frac{\Delta H}{RT^2} \qquad (8)$$

Substitute H_T and integrate, we get

$$R(\ln K) = 125{,}364\,T^{-1} + 10.272(\ln T) - 21.4(10^{-3})T/2 + 8.30(10^{-6})T^2/6 + I \qquad (9)$$

The value of I can be found if ln K is known at a given temperature, e.g., the value of ln K at 298 ^{o}K., which can be determined from the relationship shown below, is known.

$$\Delta F^{o} = -RT(\ln K) = \Delta H - T\Delta S \qquad (10)$$

$$\Delta S^{o}_{298} = \Sigma S^{o}(\text{ Products }) - \Sigma S^{o}(\text{ Reactants }) \qquad (11)$$

where S^{o} are found from Perry's Chemical Engineer's Hand Book and estimated by two different methods.(Refer to Reid, R.C. and Sherwood, T.K.; The properties of gases and liquids) At 298^{o} K.

$$R(\ln K) = \Delta S^{o}_{298} - \frac{\Delta H^{o}_{298}}{298} \qquad (12)$$

For the mentioned reaction

$$R(\ln K) = 442.46$$

Substitute this value to Equation (9) and get

$$I = -33.68$$

Hence, the equilibrium constant at any temperature can be found from the relationship :

$$4.575 \log_{10} K = 125{,}364\ T + 10.272(\ln T) - 21.4(10^{-3})T/2 + 8.30(10^{-6})T^{2}/6 - 33.68 \qquad (13)$$

C. Derivation of Free Energy Values

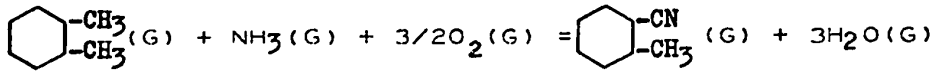
The free energy values at various temperature can be calculated from the relationship :

$$\Delta F_{T} = -RT(\ln K) = -4.575\ T\ (\log_{10} K) \qquad (14)$$

Based on the above equations thermodynamic values for different reactions were calculated from 300 - 1000^{o} K. The results are shown in following tables.

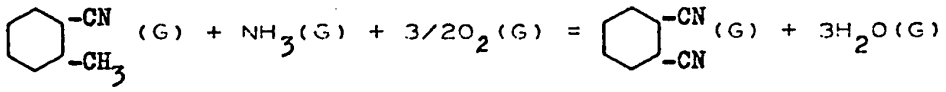
TABLE 6. THERMODYNAMIC REACTION CALCULATION

6 - 1 REACTION



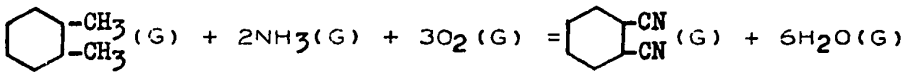
TEMPERATURE		ΔH	LOG_{10} K	ΔF
^oK	^oC	KCAL/MOLE		KCAL/MOLE
300	27	-123.17	96.11	-131.91
400	127	-122.79	73.71	-134.89
500	227	-122.56	60.30	-137.94
600	327	-122.46	51.38	-141.03
700	427	-122.47	45.01	-144.13
800	527	-122.58	40.22	-147.22
900	627	-122.77	36.50	-150.29
1000	727	-123.03	33.51	-153.33

6 - 2 REACTION



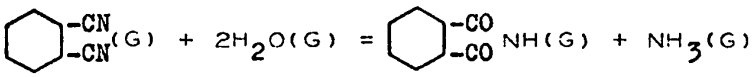
TEMPERATURE		ΔH	LOG_{10} K	ΔF
^oK	^oC	KCAL/MOLE		KCAL/MOLE
300	27	-122.73	95.75	-131.42
400	127	-122.38	73.43	-134.37
500	227	-122.16	60.06	-137.40
600	327	-122.08	51.17	-140.45
700	427	-122.11	44.81	-143.51
800	527	-122.23	40.04	-146.56
900	627	-122.43	36.33	-149.59
1000	727	-122.69	33.35	-152.60

6 - 3 REACTION



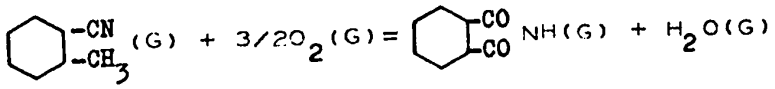
TEMPERATURE		ΔH	$LOG_{10}K$	ΔF
°K	°C	KCAL/MOLE		KCAL/MOLE
300	27	-245.90	191.86	-263.33
400	127	-245.17	147.14	-269.26
500	227	-244.72	120.37	-375.34
600	327	-244.53	102.54	-281.48
700	427	-244.57	89.82	-287.64
800	527	-574.81	80.27	-293.78
900	627	-245.20	72.83	-299.88
1000	727	-245.72	66.87	-305.93

6 - 4 REACTION



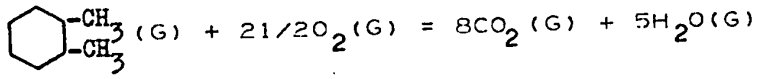
TEMPERATURE		ΔH	$LOG_{10}K$	ΔF
°K	°C	KCAL/MOLE		KCAL/MOLE
300	27	-5.65	-18.59	25.52
400	127	-6.15	-19.67	35.99
500	227	-6.41	-20.35	46.56
600	327	-6.48	-20.82	57.16
700	427	-6.37	-21.16	67.76
800	527	-6.12	-21.40	78.34
900	627	-5.75	-21.59	88.88
1000	727	-5.30	-21.72	99.37

6 - 5 REACTION



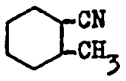
TEMPERATURE		ΔH	$LOG_{10}K$	ΔF
^oK	^oC	KCAL/MOLE		KCAL/MOLE
300	27	-128.38	77.16	-105.90
400	127	-128.52	53.76	- 98.38
500	227	-128.58	39.71	- 90.83
600	327	-128.56	30.34	- 83.29
700	427	-128.48	23.65	- 75.75
800	527	-128.35	18.64	- 68.22
900	627	-128.18	14.75	- 60.72
1000	727	-127.99	11.64	- 53.23

6 - 6 REACTION



TEMPERATURE		ΔH	$LOG_{10}K$	ΔF
^oK	^oC	KCAL/MOLE		KCAL/MOLE
300	27	-1,045.93	769.77	-1,056.51
400	127	-1,045.84	57 .26	-1,056.51
500	227	-1,046.08	464.96	-1,063.59
600	327	-1,046.62	388.72	-1,067.04
700	427	-1,047.42	334.23	-1,070.38
800	527	-1,048.43	293.33	-1,073.60
900	627	-1,049.63	261.49	-1,076.68
1000	727	-1,050.97	235.98	-1,079.61

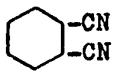
6 - 7 REACTION



(G) + $17/2O_2$(G) = $7CO_2$(G) + $3H_2O$(G) + HCN(G)

TEMPERATURE		Δ H	$LOG_{10}K$	Δ F
^oK	^oC	KCAL/MOLE		KCAL/MOLE
300	27	-844.27	621.01	-852.33
400	127	-844.26	467.23	-855.03
500	227	-844.52	374.95	-857.70
600	327	-845.02	313.40	-860.29
700	427	-845.73	269.41	-862.78
800	527	-846.61	236.38	-865.16
900	627	-847.64	210.67	-867.42
1000	727	-848.78	190.07	-869.56

6 - 8 REACTION



(G) + $13/2O_2$(G) = $6CO_2$(G) + H_2O(G) + 2HCN

TEMPERATURE		Δ H	$LOG_{10}K$	Δ F
^oK	^oC	KCAL/MOLE		KCAL/MOLE
300	27	-643.04	472.61	-648.66
400	127	-643.09	355.48	-650.53
500	227	-643.36	285.19	-652.36
600	327	-643.80	238.30	-654.12
700	427	-644.41	204.78	-655.80
800	527	-645.15	179.61	-657.38
900	627	-646.00	160.01	-658.86
1000	727	-646.93	144.31	-660.23

APPENDIX III

THE DATA OF QUANTITATIVE TREATMENTS

TABLE 7. DATA OF QUANTITATIVE TREATMENTS

TABLE 7.1

T	CT OBS	CT PRED	RESIDUALS
7.0	0.0000E 00	0.1061E-08	-0.1061E-08
5.0	0.2850E-08	0.3577E-08	-0.7269E-09
4.0	0.9890E-08	0.7320E-08	0.2570E-08
3.0	0.1587E-07	0.1367E-07	0.2205E-08
2.5	0.2299E-07	0.1987E-07	0.3025E-08
2.0	0.2566E-07	0.2627E-07	-0.6083E-09
1.5	0.4203E-07	0.3823E-07	0.3802E-08
0.8	0.5210E-07	0.6178E-07	-0.9683E-08

TABLE 7.2

T	(1-QX)OBS	(1-QX)PRED	RESIDUALS
7.0	0.0000E 00	0.8081E-02	-0.8081E-02
5.0	0.0258E-00	0.3201E-01	-0.6212E-02
4.0	0.0870E-00	0.6372E-01	0.2328E-01
3.0	0.1484E 00	0.1268E 00	0.2158E-01
2.5	0.2075E 00	0.1789E 00	0.2858E-01
2.0	0.2448E 00	0.2524E 00	-0.7621E-02
1.5	0.3930E 00	0.3561E 00	0.3688E-01
0.8	0.4872E 00	0.5766E 00	-0.8937E-01

TABLE 7.3

T	QT OBS	QT PRED	RESIDUALS
7.0	0.05100E-00	0.35064E-02	0.47494E-01
5.0	0.07040E-00	0.13885E-01	0.56515E-01
4.0	0.08470E-00	0.27598E-01	0.57102E-01
3.0	0.11830E 00	0.54554E-01	0.63746E-01
2.5	0.12660E 00	0.76158E-01	0.50442E-01
2.0	0.12800E 00	0.10493E-00	0.23068E-01
1.5	0.10090E 00	0.14020E-00	-0.39304E-01
0.8	0.09630E-00	0.17984E 00	-0.83542E-01

TABLE 7.4

T	QP OBS	QP PRED	RESIDUALS
7.0	0.1909E 00	0.1252E-01	0.1784E 00
5.0	0.3595E 00	0.4803E-01	0.3115E 00
4.0	0.3932E 00	0.9148E-01	0.3017E 00
3.0	0.3906E 00	0.1657E 00	0.2249E 00
2.5	0.3998E 00	0.2147E 00	0.1851E 00
2.0	0.3322E 00	0.2649E 00	0.6727E-01
1.5	0.2476E 00	0.2983E 00	-0.5066E-01
0.8	0.1754E 00	0.2231E 00	-0.4765E-01

TABLE 7.5

T	CX OBS	CX PRED	RESIDUALS
7.0	0.00000E 00	0.1863E-08	-0.1863E-08
5.0	0.28500E-08	0.5528E-08	-0.2678E-08
4.0	0.98900E-08	0.9522E-08	0.3678E-09
3.0	0.15970E-07	0.1640E-07	-0.5311E-09
2.5	0.22890E-07	0.2152E-07	0.1365E-08
2.0	0.25660E-07	0.2825E-07	-0.2598E-08
1.5	0.42030E-07	0.3707E-07	0.4955E-08
0.8	0.52100E-07	0.5425E-07	-0.2147E-08

TABLE 7.6

T	CT OBS	CT PRED	RESIDUALS
7.0	0.66000E-09	0.1514E-08	-0.8541E-09
5.0	0.77700E-08	0.6772E-08	0.9984E-09
4.0	0.96300E-08	0.1040E-07	-0.7659E-09
3.0	0.12650E-07	0.1289E-07	-0.2412E-09
2.5	0.13970E-07	0.1325E-07	0.7194E-09
2.0	0.13250E-07	0.1291E-07	0.3381E-09
1.5	0.10790E-07	0.1193E-07	-0.1138E-09
0.8	0.10300E-07	0.9759E-08	0.5409E-09

TABLE 7.7

T	CP OBS	CP PRED	RESIDUALS
7.0	0.24630E-07	0.2124E-07	0.3389E-08
5.0	0.39660E-07	0.4204E-07	-0.2380E-08
4.0	0.44720E-07	0.4473E-07	-0.1039E-10
3.0	0.41770E-07	0.4228E-07	-0.5110E-09
2.5	0.40800E-07	0.3913E-07	0.1671E-08
2.0	0.34400E-07	0.3469E-07	-0.2922E-09
1.5	0.26480E-07	0.2897E-07	-0.2490E-08
0.8	0.18760E-07	0.1880E-07	-0.4139E-10

TABLE 7.8

T	CD OBS	CD PRED	RESIDUALS
7.0	0.97800E-07	0.9345E-07	0.4350E-08
5.0	0.60050E-07	0.6675E-07	-0.6700E-08
4.0	0.49480E-07	0.5340E-07	-0.3920E-08
3.0	0.36650E-07	0.4005E-07	-0.3400E-08
2.5	0.32670E-07	0.3338E-07	-0.7100E-09
2.0	0.30540E-07	0.2670E-07	0.3840E-08
1.5	0.27640E-07	0.2003E-07	0.7610E-08
0.8	0.25780E-07	0.1068E-07	0.1510E-07

TABLE 7.9

T	CX	CT	CP	CD
7.0	0.18639E-08	0.15147E-08	0.21236E-07	0.93450E-07
6.5	0.24461E-08	0.23862E-08	0.28364E-07	0.86775E-07
6.0	0.32103E-08	0.35638E-08	0.34207E-07	0.80100E-07
5.5	0.42131E-08	0.50459E-08	0.38765E-07	0.73425E-07
5.0	0.55293E-08	0.67730E-08	0.42038E-07	0.66750E-07
4.5	0.72565E-08	0.86186E-08	0.44026E-07	0.60075E-07
4.0	0.95234E-08	0.10397E-07	0.44729E-07	0.53400E-07
3.5	0.12498E-07	0.11890E-07	0.44146E-07	0.46725E-07
3.0	0.16403E-07	0.12891E-07	0.42279E-07	0.40050E-07
2.5	0.21527E-07	0.13250E-07	0.39127E-07	0.33375E-07
2.2	0.25341E-07	0.13129E-07	0.36619E-07	0.29370E-07
2.0	0.28252E-07	0.12911E-07	0.34690E-07	0.26700E-07
1.8	0.31497E-07	0.12598E-07	0.32555E-07	0.24030E-07
1.5	0.37077E-07	0.11926E-07	0.28968E-07	0.20025E-07
1.2	0.43646E-07	0.11084E-07	0.24918E-07	0.16020E-07
0.8	0.54249E-07	0.97569E-08	0.19798E-07	0.10680E-07

TABLE 7.10

T	RX	RT	RP	RD
7.0	0.10134E-08	-0.14577E-08	-0.15541E-07	0.13350E-07
6.5	0.13300E-08	-0.20418E-08	-0.12971E-07	0.13350E-07
6.0	0.17454E-08	-0.26699E-08	-0.10401E-07	0.13350E-07
5.5	0.22907E-08	-0.32401E-08	-0.78308E-08	0.13350E-07
5.0	0.30063E-08	-0.36259E-08	-0.52608E-08	0.13350E-07
4.5	0.39454E-08	-0.36937E-08	-0.26908E-08	0.13350E-07
4.0	0.51779E-08	-0.33459E-08	-0.12076E-09	0.13350E-07
3.5	0.67954E-08	-0.25568E-08	0.24492E-08	0.13350E-07
3.0	0.89182E-08	-0.13957E-08	0.50192E-08	0.13350E-07
2.5	0.11704E-07	-0.19809E-10	0.75892E-08	0.13350E-07
2.2	0.13778E-07	0.82144E-09	0.91312E-08	0.13350E-07
2.0	0.15360E-07	0.13592E-08	0.10159E-07	0.13350E-07
1.8	0.17125E-07	0.18628E-08	0.11187E-07	0.13350E-07
1.5	0.20159E-07	0.25288E-08	0.12729E-07	0.13350E-07
1.2	0.23730E-07	0.30603E-08	0.14271E-07	0.13350E-07
0.8	0.29495E-07	0.35273E-08	0.16327E-07	0.13350E-07

TABLE 7.11

RX OBS	RX PRED	RESIDUALS
0.10134E-08	0.10134E-08	0.73275E-14
0.13300E-08	0.13299E-08	0.67502E-13
0.17454E-08	0.17454E-08	-0.25313E-13
0.22907E-08	0.22906E-08	0.56843E-13
0.30063E-08	0.30063E-08	0.42188E-13
0.39454E-08	0.39453E-08	0.71054E-13
0.51779E-08	0.51778E-08	0.60396E-13
0.67954E-08	0.67951E-08	0.28066E-12
0.89182E-08	0.89183E-08	-0.63949E-13
0.11704E-07	0.11704E-07	-0.17053E-12
0.13778E-07	0.13778E-07	0.15987E-12
0.15360E-07	0.15361E-07	-0.54357E-12
0.17125E-07	0.17125E-07	0.15632E-12
0.20159E-07	0.20159E-07	0.31264E-12
0.23730E-07	0.27730E-07	-0.24514E-12
0.29495E-07	0.29495E-07	-0.92371E-13

TABLE 7.12

(RX-RT) OBS	(RX-RT) PRED	RESIDUALS
0.24711E-08	0.28660E-08	-0.39490E-09
0.33717E-08	0.40503E-08	-0.67864E-09
0.44143E-08	0.54963E-08	-0.10820E-08
0.55307E-08	0.71616E-08	-0.16309E-08
0.66321E-08	0.89599E-08	-0.23278E-08
0.76391E-08	0.10763E-07	-0.31243E-08
0.85237E-08	0.12415E-07	-0.38915E-08
0.93522E-08	0.13750E-07	-0.43978E-08
0.10314E-07	0.14622E-07	-0.43084E-08
0.11724E-07	0.14931E-07	-0.32073E-08
0.12956E-07	0.14827E-07	-0.18714E-08
0.14001E-07	0.14640E-07	-0.63867E-09
0.15262E-07	0.14360E-07	0.90190E-09
0.17630E-07	0.13782E-07	0.38483E-08
0.20670E-07	0.13035E-07	0.76353E-08
0.25968E-07	0.11829E-07	0.14139E-07

TABLE 7.13

(RX-RT) OBS	(RX-RT) PRED	RESIDUALS
0.24711E-08	0.25945E-08	-0.12337E-09
0.33717E-08	0.39287E-08	-0.55697E-09
0.44143E-08	0.55752E-08	-0.11609E-08
0.55307E-08	0.74282E-08	-0.18975E-08
0.66321E-08	0.93294E-08	-0.26973E-08
0.76391E-08	0.11108E-07	-0.34690E-08
0.85237E-08	0.12618E-07	-0.40945E-08
0.93522E-08	0.13756E-07	-0.44042E-08
0.10314E-07	0.14462E-07	-0.41476E-08
0.11724E-07	0.14704E-07	-0.29802E-08
0.12956E-07	0.14623E-07	-0.16670E-08
0.14001E-07	0.14475E-07	-0.47424E-09
0.15262E-07	0.14253E-07	0.10094E-08
0.17630E-07	0.13792E-07	0.38476E-08
0.20670E-07	0.13155E-07	0.75146E-08
0.25968E-07	0.12095E-07	0.13873E-07

TABLE 7.14

(RX-RT) OBS	(RX-RT) PRED	RESIDUALS
0.24711E-08	0.10803E-08	0.13908E-08
0.33717E-08	0.17160E-08	0.16557E-08
0.44143E-08	0.25909E-08	0.18234E-08
0.55307E-08	0.37218E-08	0.18089E-08
0.66321E-08	0.50931E-08	0.15390E-08
0.76391E-08	0.66512E-08	0.98788E-09
0.85237E-08	0.83101E-08	0.21357E-09
0.93522E-08	0.99736E-08	-0.61837E-09
0.10314E-07	0.11556E-07	-0.12416E-08
0.11724E-07	0.13059E-07	-0.13354E-08
0.12956E-07	0.13975E-07	-0.10194E-08
0.14001E-07	0.14637E-07	-0.63603E-09
0.15262E-07	0.15386E-07	-0.12420E-09
0.17630E-07	0.16840E-07	0.78970E-09
0.20670E-07	0.19152E-07	0.15181E-08
0.25968E-07	0.26384E-07	-0.41558E-09

APPENDIX IV

CALIBRATION CURVES FOR ROTAMETERS

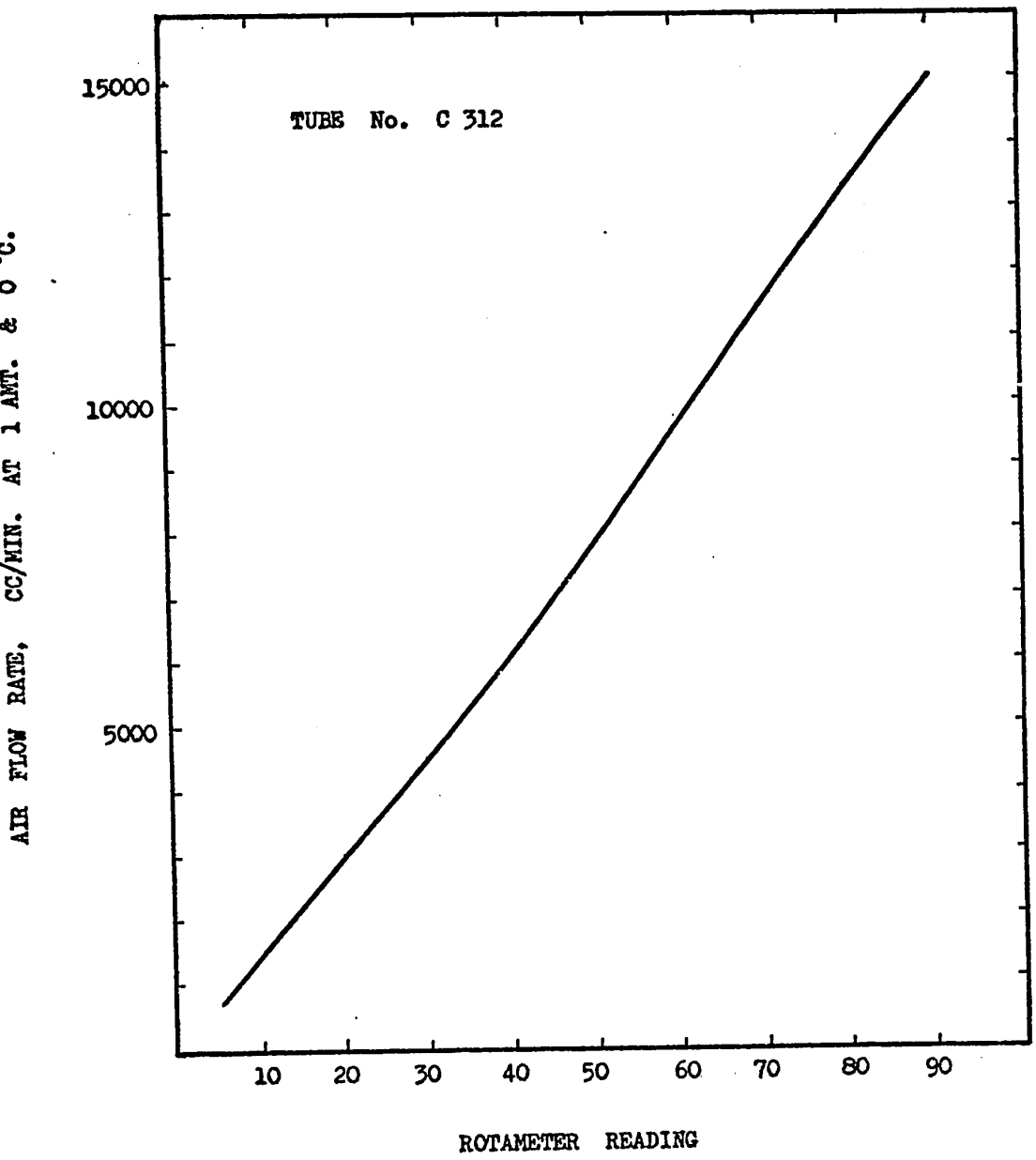


FIGURE 9. CALIBRATION CURVE FOR AIR ROTAMETER

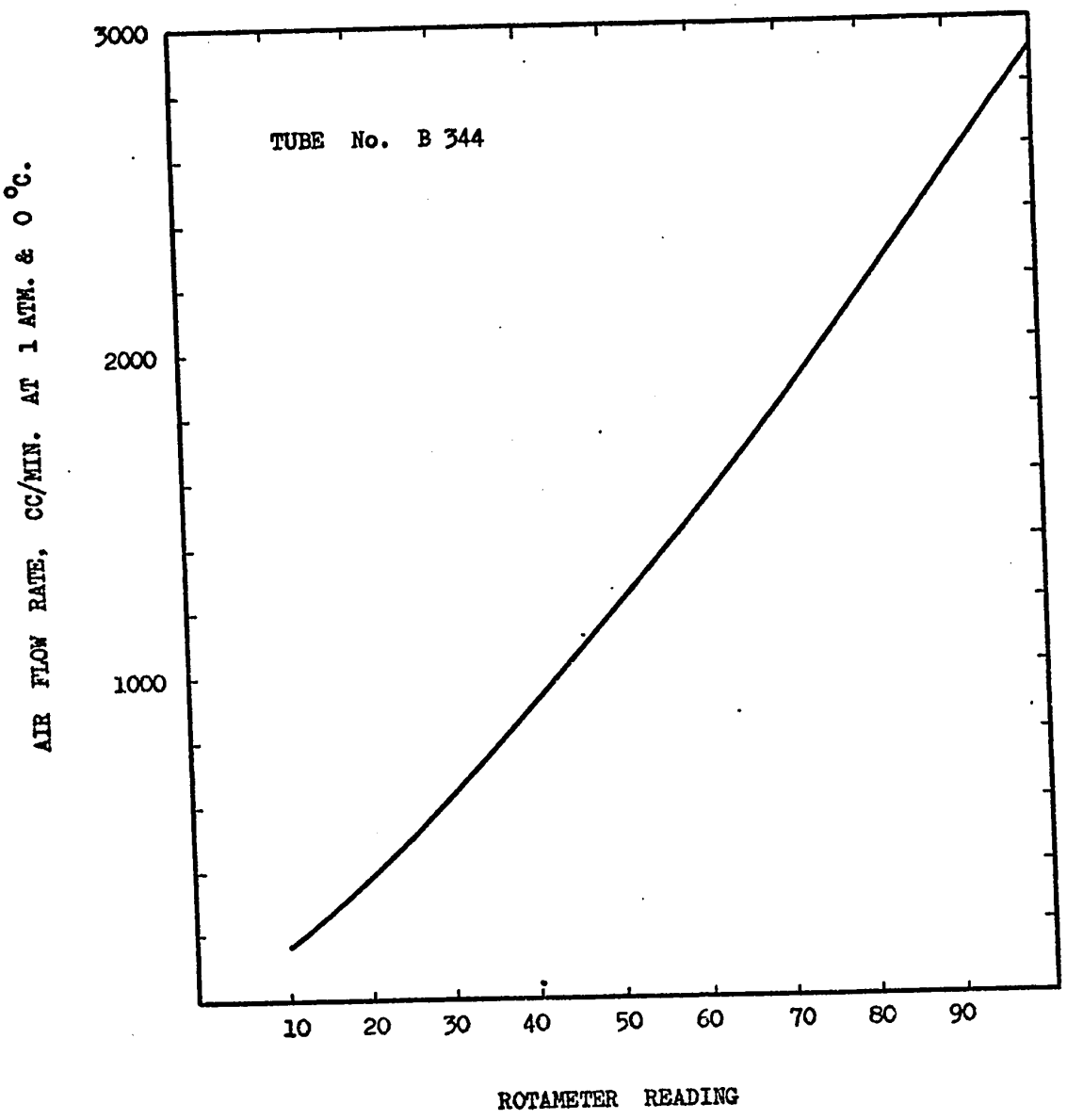


FIGURE 10. CALIBRATION CURVE FOR AIR ROTAMETER

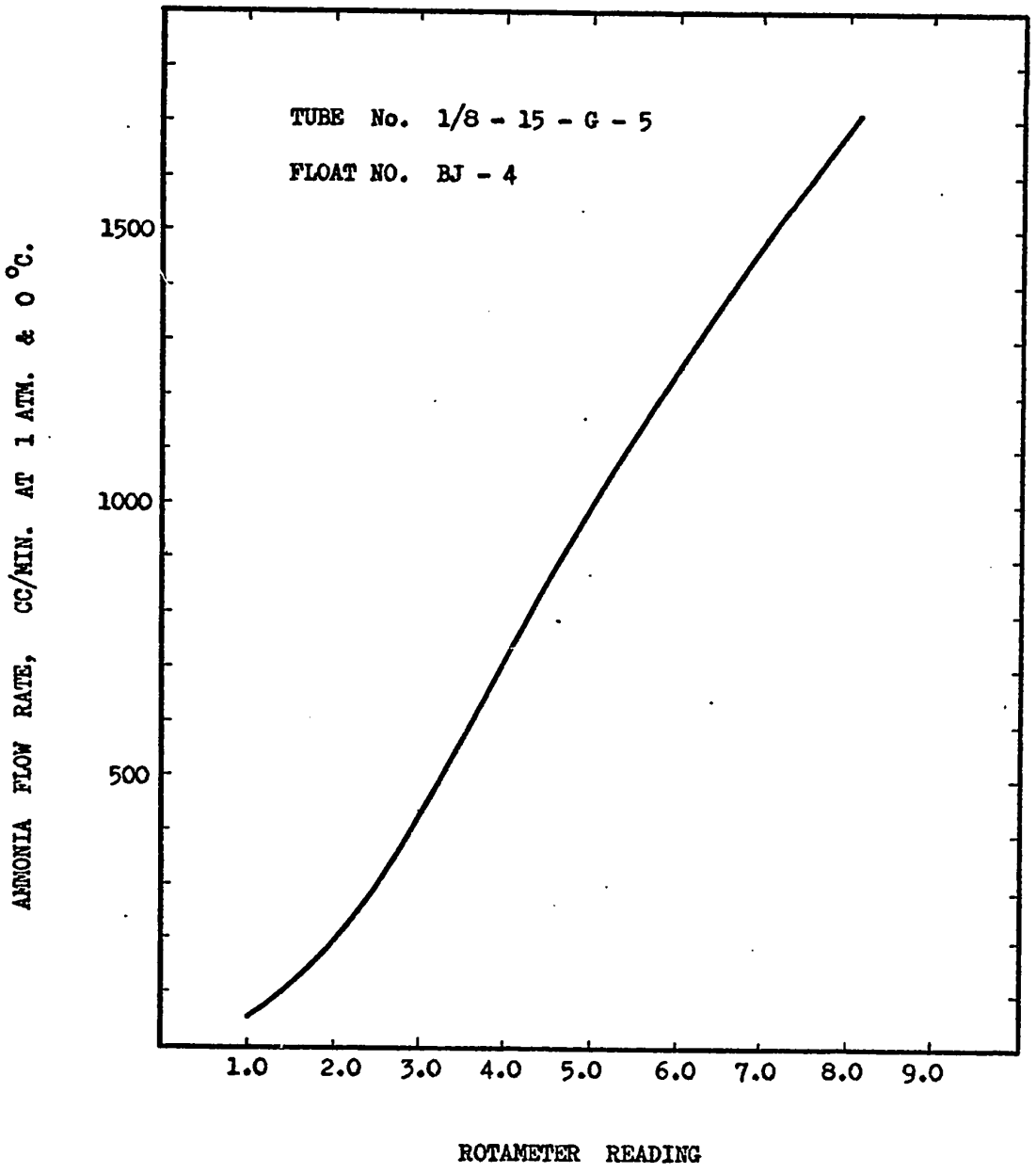


FIGURE 11. CALIBRATION CURVE FOR AMMONIA ROTAMETER

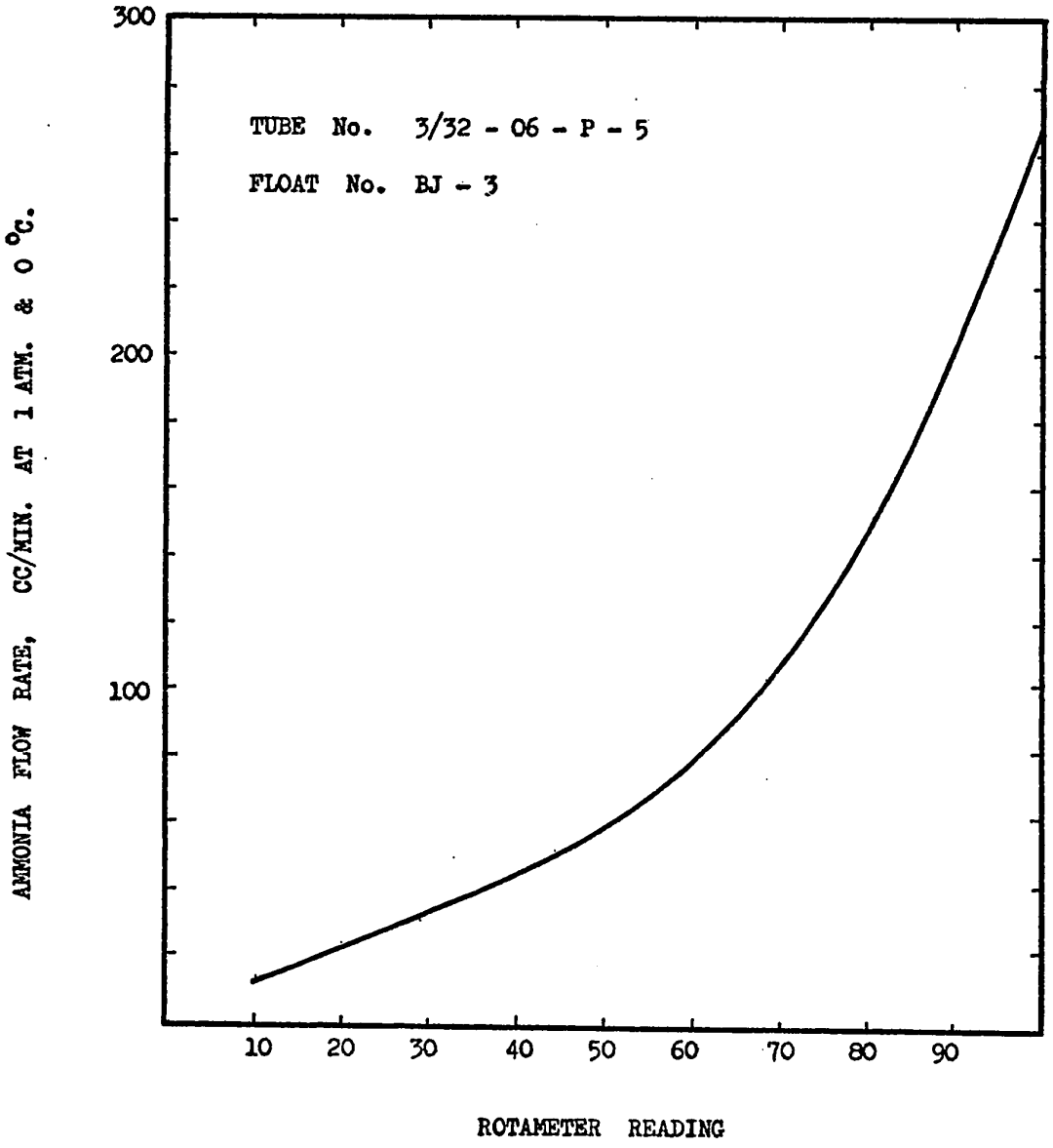


FIGURE 12. CALIBRATION CURVE FOR AMMONIA ROTAMETER

APPENDIX V

ECONOMIC ASPECTS OF XYLENES

Table 8. The Current Prices of C_8 Aromatics

	Approximate Prices of C_8 Aromatics, ¢/lb		
	1958	1967	1970
use, or component in hydroformer product, as a component of gasoline			2.0
as solvent	3.3	2.5	2.5
o-xylene	6.0(1960)	3.0	3.0
ethylbenxene	8.0	4.0	4.0
p-xylene	16.0	8.0	7.0
m-xylene (higher than 95 %)			14 - 16

Table 9. Estimated Aromatics Demand, Thousands of Metric Tons (2204 lb)

	1970		1975		1980	
Country	Benzene	o,p-Xylene	Benzene	o,p-Xylene	Benzene	o,p-Xylene
U.S.A.	3500	650	4550	1300	5600	2050
W.Europe	2750	740	4200	1140	5600	1725
Japan	850	235	1400	525	2000	900
other *	500	65	1000	165	1800	325
Total	7600	1690	11,150	3130	15,000	5000

* Free world

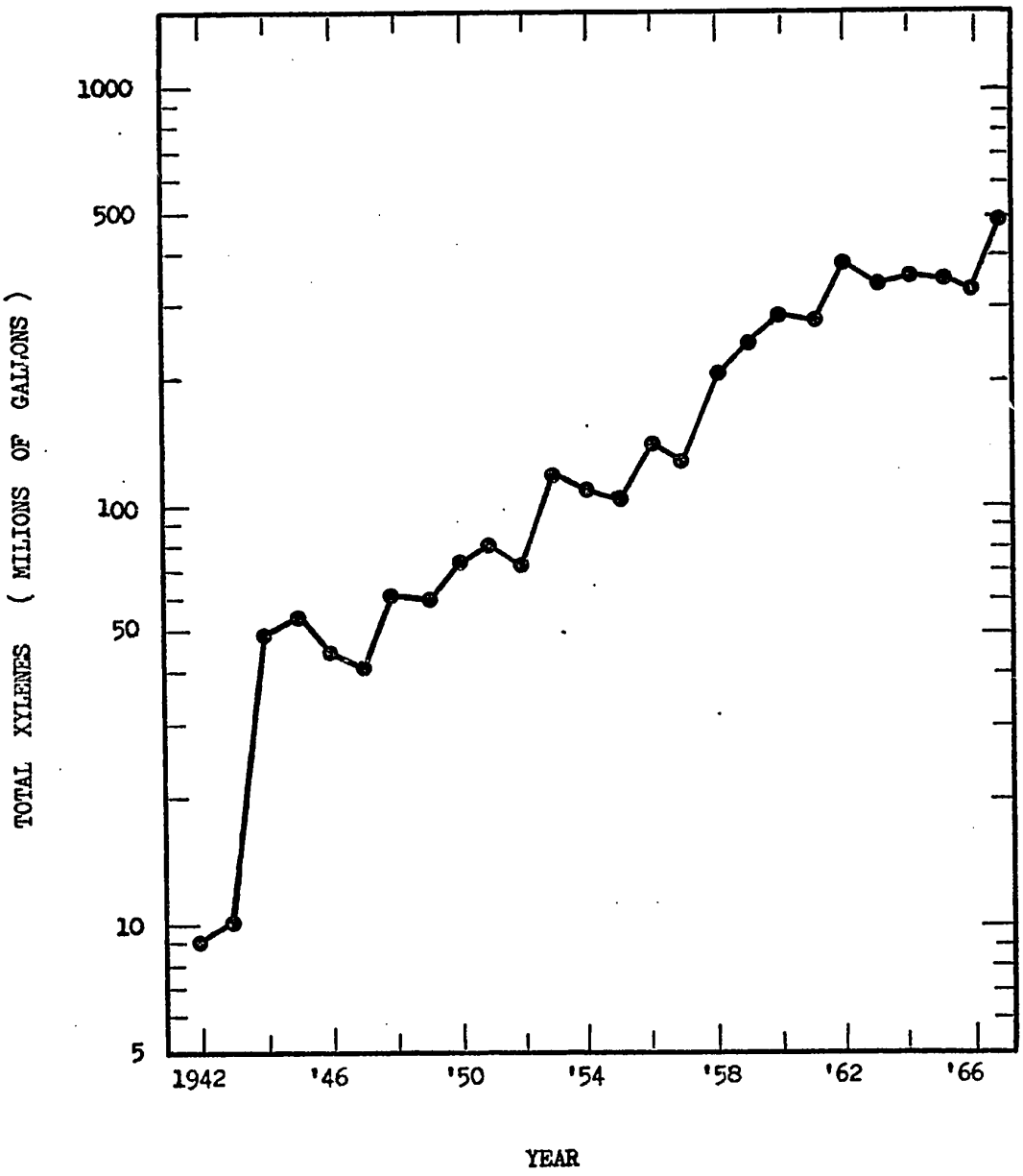


FIGURE 13. PRODUCTION OF XYLENES

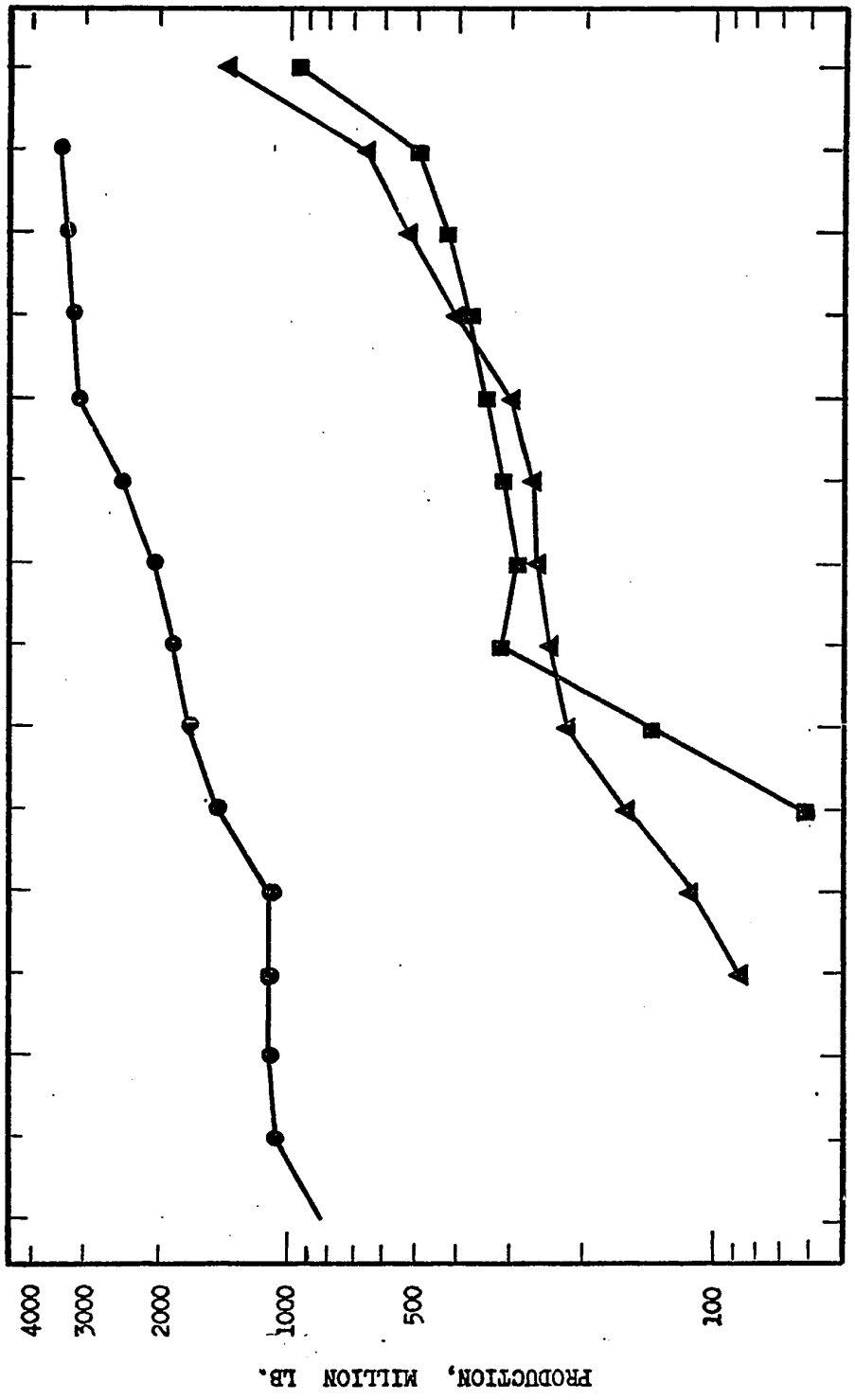


FIGURE 14. PRODUCTION OF INDIVIDUAL C_8 ISOMERS

APPENDIX VI

EQUIPMENT SPECIFICATIONS

EQUIPMENT SPECIFICATIONS

1. Air Filter

Make :	Trerice and Company
Type :	Model No. 40
Capacity :	275 CMF at 80 - 100 lbs air (Max)
Maximum pressure :	300 psig
Filter screen :	stone

2. Low Pressure Regulator (PR1 in Figure 1)

Make :	Matheson of Canada Ltd.
Type :	Model No. 70A
Inlet pressure :	Maximum 250 psig
Outlet pressure :	5 - 10 psig
Delivery pressure gauge :	0 -30 psig
Inlet hose connection :	Matheson reinforced butyl rubber hose to withstand 2500 psig

3. Low Pressure Regulator (PR2 in Figure 1)

Make :	Matheson of Canada Ltd.
Type :	Model No. 71A
Inlet pressure :	Maximum 250 psig
Outlet pressure :	5 - 10 psig
Delivery pressure gauge :	0 - 15 psig

4. Air Rotameter (R1 in Figure 1)

Make :	Roger Gilmont Instruments, Inc.
Tube No. :	C 312
Scale :	
Capacity :	35 CFH air at 0° C. and 1 atm.

5. Air Rotameter (R1 in Figure 1)

Make :	Roger Gilmont Instruments, Inc.
Tube No. :	B 344
Scale :	
Capacity :	3000 CCM air at 0° C. and 1 atm.

6. Air Rotameter (R2 in Figure 1)

Make :	Roger Gilmont Instruments, Inc.
Tube No. :	
Scale :	
Capacity :	

7. Ammonia Rotameter (R3 in Figure 1)

Make :	Schutte and Koerting Co.(Canada) Ltd.
Type :	'Lo Flo' rotameter, SK - 1875V series
Tube No. :	SK-1/8-15-G-5
Float No. :	BJ-4
Scale :	5 inch
Capacity :	1460 CCM air at 70° F. and 14.7 psia

Maximum operating pressure: 300 psig

Max. operating temperature: 200° F.

8. Ammonia Rotameter (R3 in Figure 1)

Make :	Schutte and Koerting Co. (Canada)Ltd.
Type :	'Lo Flo' rotameter, SK - 1875V series
Tube No. :	SK-3/32-06-P-5
Float No. :	BJ-3
Scale :	5 inch
Capacity :	97 CCM at 70° F. and 14.7 psia
Max. operating pressure :	300 psig
Max. operating temp. :	200° F.

9. Air Control Valves (NV1 and NV2 in Figure 1)

Make :	Matheson of Canada Ltd
Type :	Model No. 940B (Instrument type metering valve)
Body :	Brass
Packing :	Buna - N

10. Check Valves (CV1, CV2, and CV3 in Figure 1)

Make :	Matheson of Canada Ltd.
Capacity :	100 SCFH air at 10 psig inlet pressure
Max. Pressure :	2000 psig

Duty	Model	Material of Construction
Air (CV1)	400-X	Brass, neoprene o-ring, stainless steel spring
Ammonia (CV2)	400-X	Stainless steel 303, viton-o-ring, stainless steel spring
o-Xylene (CV3)	400-X	stainless steel 303, viton-o-ring, stainless steel spring

11. Selector Switch

Make : Thermovolt

Type : Multipolar rotary switch - UPMF 16/2 (16 point selection)

12. Electrical Heating Units

Make : Lindberg and Heavy Duty

Type : Heavy semi-cylindrical units for 1000° C

Duty	Model	Diameter	Length	Watts*	Connection
Preheater	50231	2-3/8"	12"	1400	parallel
carburettor	50221	2-3/8"	18"	1000	parallel
Reactor top	73-S	1-1/4"	4"	210	series
Reactor middle	73-S	1-1/4"	4"	210	series
Reactor bottom	73-S	1-1/4"	4"	210	series

* 2 pieces at 115 volts

13. Variable Transformers

Duty	Make	Type	Max. amps	Requirement amps
preheator	General Radio	W5MMB	40	12.2
carburettor	Powerstat	116B	10	8.7
reactor top	Powerstat	116	8	1.8
reactor middle	Powerstat	116B	10	1.8
reactor bottom	Powerstat 11	116	8	1.8
heating tapes				
preheater to carburetor	Powerstat	116	8	3.5
carburetor to reactor	General Radio	W5MT	5	1.0
reactor to cooling trap	General Radio	W5MT	5	1.0
feeding tank to line	General Radio	W5MT	5	1.0

14. Thermocouples (TC1 and TC4)

Make : Thermocouple Products

Type : Chromel - alumel, 1/16" O. D.

Junction : grounded

15. Thermocouples (TC2, TC3, TC8, TC13 and TC14)

Make : Thermocouple Products

Type : Chromel - alumel, 1/16" O. D.

Junction : ungrounded

16. Thermocouples (TC5, TC6, TC7, TC9, TC10, TC11, TC12 and reference)

Make : Thermoelectric (Canada) Ltd.

Type : ISA-K, Chromel - alumel, 5K1100A, stainless steel 304 sheath, 1/25" O. D.

Junction : ungruonded

VITA AUCTORIS

1930	Born at Canton,China on Feb. 8.
1949	Graduated from Pui-Ying Middle School, Canton, China.
1961	Recieved Bachelor of Engineering (Chemical) from Tientsin University, Tientsin, The People's Republic of China.
1969	Accepted into the Graduate School of the University of Windsor, Windsor, Ontario as a Candidate for the Degree of Master of Applied Science in Chemical Engineering.